Rhodium(I)-Assisted Stereoselective Coupling of an Alkyl, Aryl or Vinyl Group with a Vinylidene Ligand: A Novel Synthetic Route to π-Allyl and π-Butadienyl Rhodium Complexes

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

Dedicated to Professor Wolfgang Beck on the occasion of his 65th birthday

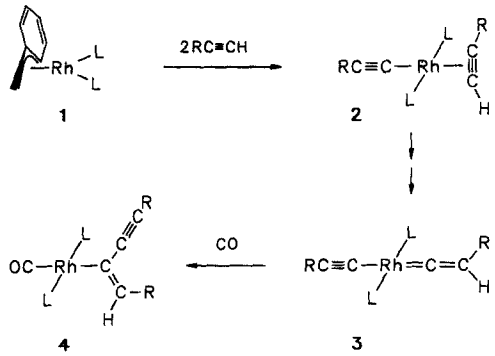
Abstract: In the first part of this work, a general method for the preparation of aryl, methyl, vinyl and alkynyl(vinylidene)rhodium(I) complexes *trans*-[Rh(R′)(=C=CHR)($P\mathit{i}Pr_3$)$_2$] (**8**–**14**, **18**–**22**) and *trans*-[Rh(R′)(=C=CMe_2)($P\mathit{i}Pr_3$)$_2$] (**16**, **17**) from the corresponding chloro(vinylidene) derivatives and Grignard reagents is described. Whilst compounds **8** and **10**–**13** react with pyridine to give *trans*-[Rh(C≡CR)(py)($P\mathit{i}Pr_3$)$_2$] (**23**–**25**) by elimination of R′H, treatment of **8**–**11**, **16**, and **18** with carbon monoxide yields the square-planar η^1-vinyl and η^1-butadienylrhodiumcarbonyl complexes *trans*-[Rh{η^1-(*Z*)-C(R′)=CHR}(CO)($P\mathit{i}Pr_3$)$_2$] (**27**–**32**). The reaction of **8** or **18** with methyl or *tert*-butylisocyanide leads stereoselectively to the isocyaniderhodium(I) compounds *trans*-[Rh{η^1-(*Z*)-C(R)=CHPh}(CNR′)($P\mathit{i}Pr_3$)$_2$] (**33**–**35**). Acid-induced cleavage of the rhodium–carbon σ bond of **27**, **30**, or **31** with CH_3CO_2H gives *trans*-[Rh(η^1-O_2CCH_3)(CO)($P\mathit{i}Pr_3$)$_2$] (**38**) and the corresponding olefin or diene, respectively. In the absence of a Lewis base such as pyridine, CO, or CNR′, compounds **18**–**20** rearrange in benzene at 40–50 °C to afford the isomeric π-allyl complexes [Rh(η^3-1-RC_3H_4)($P\mathit{i}Pr_3$)$_2$] (**40**–**42**) almost quantitatively. The vinyl(vinylidene) compounds **11** and **12** also undergo an intramolecular rearrangement that leads to the η^3-2,3,4-butadienyl- or to the alkynyl(ethene)rhodium(I) isomers, depending on the reaction conditions. In an analogous manner to the η^1-vinyl- and η^1-butadienyl(carbonyl) derivatives **27**, **30**, and **31**, the π-allyl and π-butadienyl complexes also react with acetic acid to give [Rh(η^2-O_2CCH_3)($P\mathit{i}Pr_3$)$_2$] (**47**) and the respective olefin.

Keywords
allyl complexes · butadienes · C–C coupling · rhodium · vinylidene complexes

Introduction

Recently we reported that the rhodium-mediated coupling of two alkyne molecules can lead to the formation of either enynes or butatrienes, provided that the reaction proceeds via an alkynyl(vinylidene) complex as a common intermediate.[1] The individual alkynyl(vinylidene)rhodium derivatives **3** are formed by treating the η^3-benzyl compound **1** with two equiv of the alkyne; in the presence of CO, they react by the coupling of two C_2 units to give the enynyl complexes **4** almost quantitatively (Scheme 1).[1, 2]

Since to the best of our knowledge examples of an *intramolecular* migration of a metal-bonded organic group to a vinylidene ligand are very rare,[3] we were interested to find out whether, in analogy to compounds **2**, the corresponding alkyl-, aryl-, and vinyl(vinylidene)rhodium complexes could be prepared, and if so, whether they also reacted by C–C coupling to give substituted vinyl- and butadienylmetal derivatives. Of course, we had to find a synthetic route other than that used for the preparation of **3** and considered the chloro(vinylidene) compounds *trans*-[RhCl(=C=CHR)($P\mathit{i}Pr_3$)$_2$][4] to be suitable starting materials.



Scheme 1. L = $P\mathit{i}Pr_3$.

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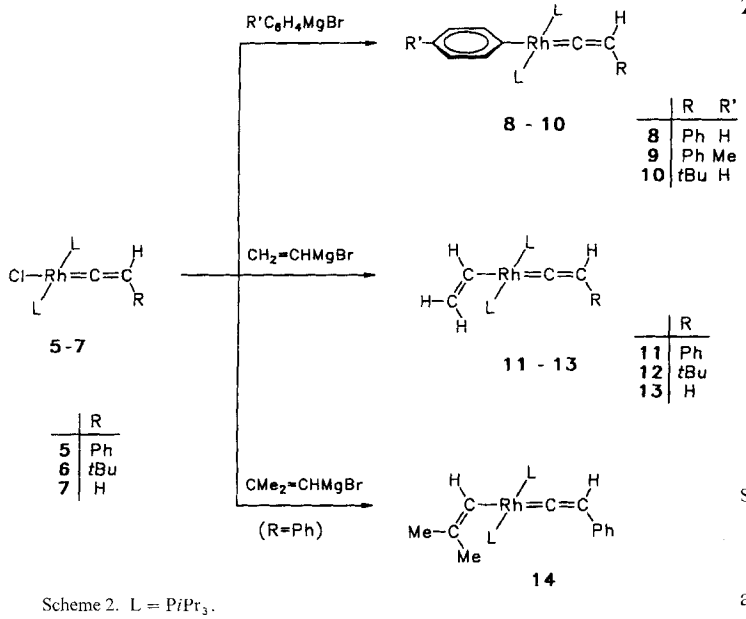
In this paper we describe the synthesis of square-planar alkyl-, aryl-, and vinyl(vinylidene)rhodium complexes *trans*-[Rh(R')(=C=CHR)($P i Pr_3$)$_2$], the routes to couple the two carbon ligands in the presence or in the absence of a Lewis base, and the smooth and stereoselective generation of substituted olefins and dienes by acid-induced cleavage of the newly formed Rh–vinyl, Rh–allyl and Rh–butadienyl bonds. Moreover, we illustrate that some of the title complexes isomerize to give two different types of products, depending on whether they react in solution or in the solid phase, which cannot be interconverted into each other. Part of the results have already been communicated.[5]

Results and Discussion

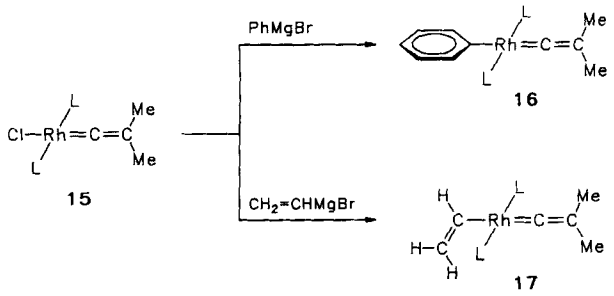
Reactions of the chloro(vinylidene)rhodium(I) complexes with Grignard reagents: Compounds **5–7** (Scheme 2), which are unsuitable starting materials for the synthesis of half-sandwich



Scheme 2. L = $P i Pr_3$.

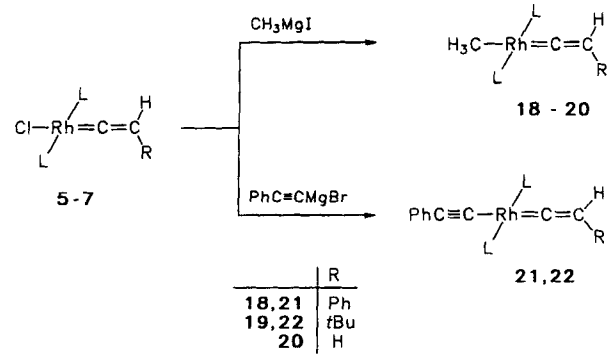
type complexes [$C_5H_5Rh(=C=CHR)(P i Pr_3)$] because of the slow rate of substitution of Cl^- by $C_5H_5^-$,[6] react with aryl or vinyl Grignard reagents in ether/THF to give the aryl- and vinylrhodium(I) derivatives **8–14** in good to excellent yield. The most characteristic feature of the spectroscopic data of **8–14** is the low-field position of the resonance of the vinylidene α-carbon atom in the ^{13}C NMR spectra that appears at $\delta = 290-300$ (in C_6D_6) and shows a strong Rh–C coupling of about 47 Hz. Since the ^{31}P NMR spectra of **8–14** display only one signal (doublet) with a chemical shift similar to that of the starting materials **5–7**,[4] there is no doubt that the two phosphine ligands are *trans* disposed.

The dimethylvinylidene complex **15**, which is accessible by an unexpected route from [$RhCl(P i Pr_3)_2]_2$, $Me_2C=CHBr$, and two equivalents of Na,[7] behaves similarly to **5–7**. On treatment with PhMgBr or $CH_2=CHMgBr$ it affords the phenyl- and vinylrhodium(I) compounds **16** and **17** (Scheme 3) in about 80% yield. Whilst in the ^1H NMR spectra of **11–13**, the signal of the Rh–C*H* proton shows a complex pattern due to coupling to rhodium, to the two phosphorus nuclei, and to the chemically inequivalent vinylic CH_2 protons, the resonance of the Rh–C*H* proton in the spectrum of **17** appears as a clean doublet of doublet of doublet of triplets at $\delta = 7.90$ (in C_6D_6).



Scheme 3. L = $P i Pr_3$.

In order to synthesize the methylrhodium(I) derivatives **18–20** (Scheme 4), the procedure followed for the preparation of the aryl and vinyl compounds **8–14** has to be modified. If the starting materials **5–7** were reacted in benzene with a solution of CH_3MgI in ether, a mixture of products was formed, which could not be completely separated into the single components. Therefore, the method of choice is to treat a *solid* sample of CH_3MgI, obtained after removing the solvent from a solution of CH_3MgI in ether, with a solution of **5**, **6**, or **7** in toluene at $-30\,^\circ C$. Upon workup, deeply colored crystalline materials of composition *trans*-[$Rh(CH_3)(=C=CHR)(P i Pr_3)_2$] are obtained in 80–90% yield. In contrast to the related compounds **8–14**, the methyl complexes **18–20** are only stable as solids and slowly decompose in solution. For this reason, only the ^{13}C NMR spectrum of **18** could be measured at room temperature. In addition to the signals for the phosphine and vinylidene carbon atoms, it shows a doublet of triplets at $\delta = -1.7$, which is assigned to the metal-bonded CH_3 carbon atom.



Scheme 4. L = $P i Pr_3$.

The alkynyl(vinylidene)rhodium(I) complexes **21** and **22**, that is, the analogues of compound **3**, are also accessible by the Grignard route. The advantage of this method over that shown

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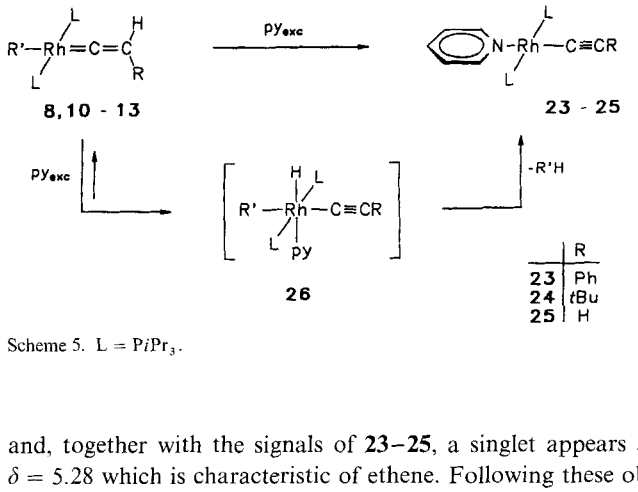
in Scheme 1 is that derivatives can be obtained with different groups R and R′ at the alkynyl and the vinylidene ligand. This is illustrated by the preparation of **22**. In addition, the formation of **22** from **10** and PhC≡CMgBr indicates that the C=CH*t*Bu moiety is not involved in the replacement process, because otherwise the *trans*-[Rh(C≡C*t*Bu)(=C=CHPh)(P*i*Pr$_3$)$_2$] isomer, which we assume is thermodynamically favored, would be produced.

Reactions of the vinylidene complexes *trans*-[Rh(R′)(=C=CHR)(P*i*Pr$_3$)$_2$] with Lewis bases: In our recent work on the reactivity of the vinylidene derivatives *trans*-[Rh(C≡CR)(=C=CHR)(P*i*Pr$_3$)$_2$],[1, 8] we found that on treating these compounds with pyridine the bis(alkynyl)hydridorhodium(III) complexes [RhH(C≡CR)$_2$(py)(P*i*Pr$_3$)$_2$] are formed. They are significantly more stable than the related compounds [RhH(C≡CR)Cl(py)(P*i*Pr$_3$)$_2$], which readily lose pyridine and regenerate the starting materials *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$].[4, 6, 9]

The vinylidene complexes **8** and **10–13** described in this work react with pyridine somewhat differently. Instead of the expected rhodium(III) species [RhH(R′)(C≡CR)(py)(P*i*Pr$_3$)$_2$], the square-planar compounds *trans*-[Rh(C≡CR)(py)(P*i*Pr$_3$)$_2$] (**23–25**) are obtained. They have been identified by comparison of their IR and NMR data with those of authentic samples, which were prepared either by elimination of HCl from [RhH(C≡CR)Cl(py)(P*i*Pr$_3$)$_2$][6] or by ligand replacement from *trans*-[Rh(C≡CR)(C$_2$H$_4$)(P*i*Pr$_3$)$_2$] and pyridine.[8]

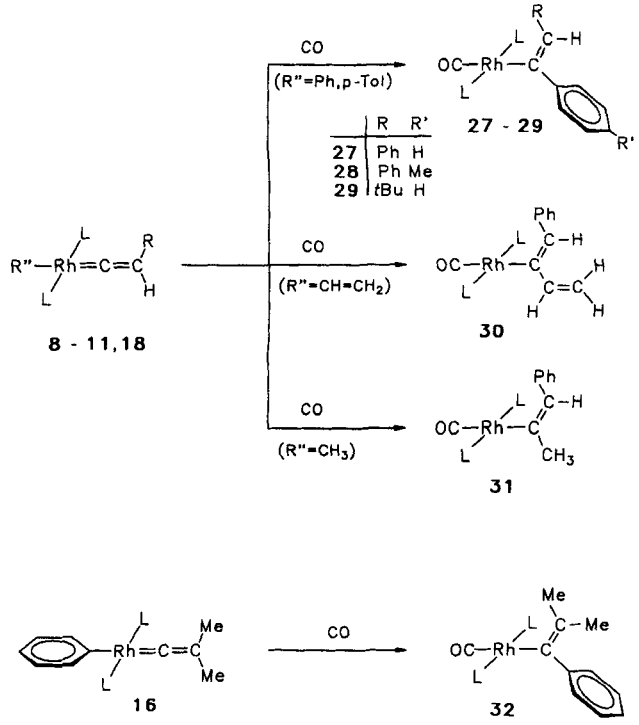
If the reaction of **11** with pyridine in C_6D_6 is studied in an NMR tube, a weak signal is initially observed in the ^{1}H NMR spectrum at $\delta \approx -17$, which is tentatively assigned to the octahedral intermediate **26** by comparison with the spectra of [RhH(C≡CR)(X)(py)(P*i*Pr$_3$)$_2$] (X = Cl, C≡CPh, C≡C*t*Bu) (Scheme 5). The high-field resonance disappears quite rapidly



Scheme 5. L = P*i*Pr$_3$.

and, together with the signals of **23–25**, a singlet appears at $\delta = 5.28$ which is characteristic of ethene. Following these observations, we assume that the different types of four-coordinate vinylidenerhodium(I) complexes *trans*-[RhX(=C=CHR)(P*i*Pr$_3$)$_2$], where X is chloride, alkynyl, aryl, vinyl, or methyl, behave quite similarly towards pyridine; and that the first step of the reactions involves a 1,3-H migration from the vinylidene β-carbon atom to the metal. Obviously, the stability of the rhodium(III) derivatives [RhH(C≡CR)(X)(py)(P*i*Pr$_3$)$_2$] depends considerably on the nature of the ligand X, whereby the extremes are probably for X = C≡CR (highest stability) and C_6H_5 or CH_3 (lowest stability).

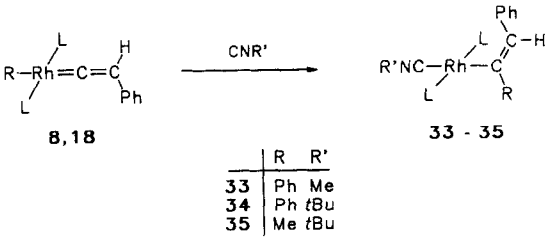
The reactions of the aryl-, vinyl-, and methyl(vinylidene) compounds **8–11**, **16**, and **18** with π-acceptor ligands follow a different pathway. When a slow stream of carbon monoxide is passed for ≈10 sec through a solution of **8–11**, **16** or **18** in toluene at low temperature (−30 to −100 °C), a characteristic change of color from violet to yellow occurs and, after recrystallization from acetone, yellow crystalline solids of composition **27–32** (Scheme 6) are isolated in almost quantitative yield.



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

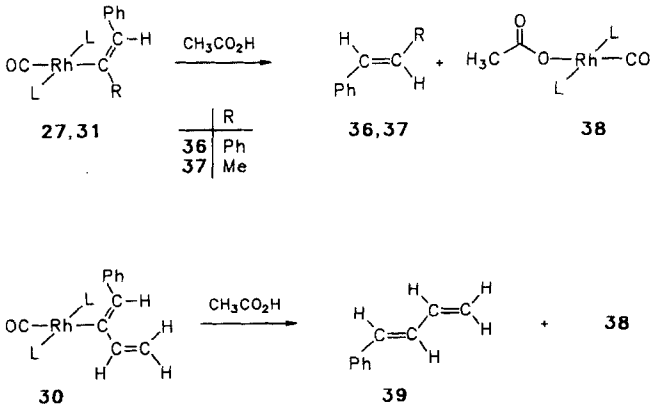
Their IR spectra show a strong band at 1925–1945 cm^{-1}, which is assigned to a C≡O stretching frequency. Since in the ^{1}H NMR spectra of **27–31** the chemical shift of the signal of the vinylic =CH proton is quite similar to that found for the enynyl complexes *trans*-[Rh{C(C≡CR)=CHR}(CO)(P*i*Pr$_3$)$_2$],[1, 8b] we assume that the *Z* isomers having the substituents R and R′ in a *trans* orientation at the C=C bond were exclusively formed. With regard to the structure of **32**, it is interesting to note that the ^{1}H NMR spectrum (in C_6D_6) displays *two* distinct signals for the =C(CH$_3$)$_2$ protons at $\delta = 2.25$ and 2.02. This indicates that the methyl groups are stereochemically different. In contrast to compounds such as *trans*-[Rh(C$_6$H$_5$)(CO)(P*i*Pr$_3$)$_2$] and *trans*-[Rh(CH=CH$_2$)(CO)(P*i*Pr$_3$)$_2$,[10] the methyl groups of the triisopropylphosphine ligands in **32** are diastereotopic and give rise to two doublets of virtual triplets at $\delta = 1.22$ and 1.16. In agreement with previous studies,[1, 8] we interprete this finding by assuming a hindered rotation of the vinylic ligand around the Rh–C σ bond, probably caused by the steric requirements of the bulky phosphines and the substituents at the C=C bond.

The reactions of **8** and **18** with methyl- or *t*-butylisocyanide also proceed selectively to furnish the substituted isocyanide-(vinyl)rhodium(I) complexes **33–35** (Scheme 7) in 70–80% yield. The yellow crystalline materials are thermally somewhat less stable than the CO derivatives **27–31** and slowly decompose in solution. Since the NMR spectroscopic data are in good agreement with those of **27**, **29**, and **31**, there is no doubt that the groups R and C_6H_5 at the C=C bond are also *trans* disposed.



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

The stereochemical arrangement of the vinylic rhodium(I) compounds, at least for the carbonyl derivatives **27**, **30**, and **31**, has also been confirmed by cleavage reactions with acetic acid in benzene. At room temperature, the *E* olefins **36**, **37**, and **39** are formed (Scheme 8) besides the acetato complex **38**[11] and



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

identified by NMR spectroscopy.[12] Under the chosen reaction conditions, there is no rearrangement of *E* to *Z* isomers. In this context it should be noted that on treatment of *trans*-[Rh{η^1-(*E*)-C(CO$_2$Me)=CHCO$_2$Me}(CO)(PPh$_3$)$_2$] with HCl, a stereoselective reaction also occurs which gives dimethylmalonate as the sole olefinic product.[13]

The molecular structure of complex 30: In order to confirm the configuration of the rhodium–butadienyl fragment, a single-crystal X-ray structural analysis of **30** was performed. The SCHAKAL drawing (Figure 1) reveals that the coordination geometry around the rhodium center is square-planar with both the phosphine ligands and the chloride and the butadienyl moiety in a *trans* disposition. Whilst the Rh–P distances are almost identical (see legend to Figure 1), the P-Rh-P unit is slightly bent. This is probably due to steric hinderance between the isopropyl and butadienyl groups. The Rh–C1 distance of 2.088(5) Å is somewhat longer than that in the octahedral butadienylrhodium(III) complex [Rh(η^2-O$_2$CCH$_3$)(C≡CCO$_2$Me)-{C(CH=CHCO$_2$Me)=CHCO$_2$Me}(P*i*Pr$_3$)$_2$] (2.015(9) Å)[14] and corresponds to that found for Rh–C(C_6H_5) in [C_5Me$_5$Rh(C_6H_5)(PPh$_3$)Br] (2.08(1) Å).[15] The C–C bond lengths of the metalated C4 ligand lie between 1.299(7) Å (C2–C3) and 1.470(6) Å (C1–C2) and are analogous to those of related η^1-butadienylrhodium,[14] -iridium,[3c] and -ruthenium complexes.[16] The C4-C1-C2-C3 torsional angle is 46.95° and thus similar to that determined recently for the cobalt compound [Co{C(CH=CH$_2$)=CH$_2$}(NC$_5$H$_4$-4-*t*Bu)(DMG)$_2$] (54.5°).[17]

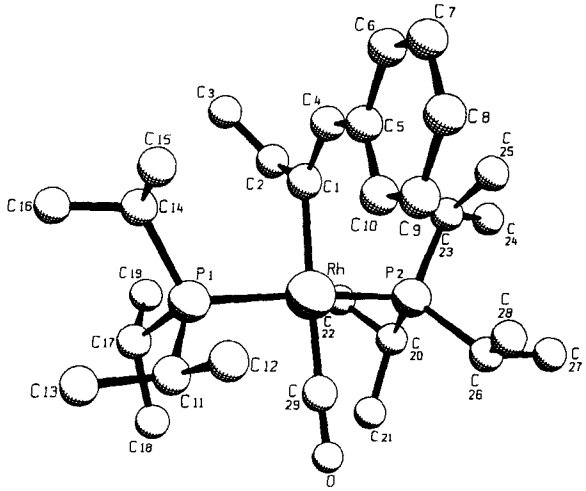


Fig. 1. Molecular structure of **30**. Principal bond lengths [Å] and angles [°], with estimated standard deviations in parentheses: Rh–P1 2.338(1), Rh–P2 2.340(1), Rh–C1 2.088(5), Rh–C29 1.815(6), C1–C2 1.470(6), C2–C3 1.299(7), C1–C4 1.356(6), C29–O 1.171(6); P1-Rh-P2 167.73(4), P1-Rh-C1 91.4(1), P2-Rh-C1 91.5(1), P1-Rh-C29 88.8(2), P2-Rh-C29 89.1(2), C1-Rh-C29 175.7(2), Rh-C1-C2 116.5(4), Rh-C1-C4 128.1(4), C1-C2-C3 127.0(6), C2-C1-C4 115.4(5), C1-C4-C5 129.7(5), Rh-C29-O 175.2(5).

C–C coupling reactions of the vinylidene complexes *trans*-[Rh(R')(=C=CHR)(P*i*Pr$_3$)$_2$] in the absence of Lewis bases: Following the observation that compounds such as **18–20** are not stable in solution but do not decompose as solids stored under argon, we discovered that a coupling of the two C-bonded ligands is possible even *without* the presence of a supporting Lewis base. If a solution of **18**, **19**, or **20** in benzene is stirred at room temperature for 12 h, a change of color from deep blue or violet to yellow or orange occurs and crystalline products of general composition [Rh(η^3-CH$_2$CHCHR)(P*i*Pr$_3$)$_2$] (**40–42**) are isolated in 70–80% yield. The parent derivative **42** is already known and has been prepared either from [Rh(η^3-C_3H_5)(η^4-C_8H_{12})] (generated in situ) and P*i*Pr$_3$, or more directly from [RhCl(P*i*Pr$_3$)$_2$]$_2$ and C_3H_5MgBr.[18] The ^{1}H NMR spectra of the phenyl- and *tert*-butylallyl complexes surprisingly reveal that in **40** the allylic unit is present in the *syn*[19] and in **41** in the *anti* configuration (see Scheme 9). Characteristic features are the different H–H coupling constants between the central allylic

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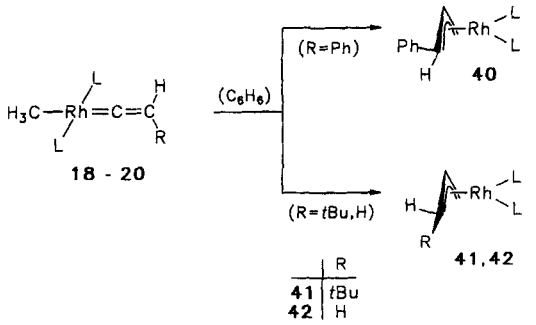
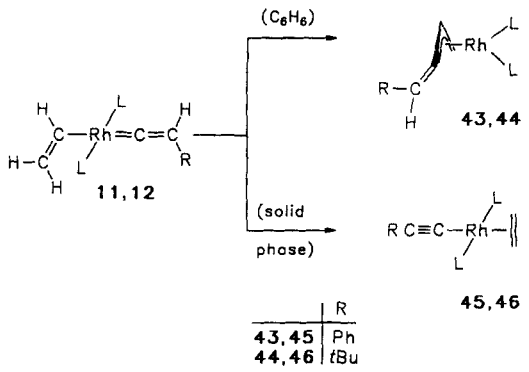


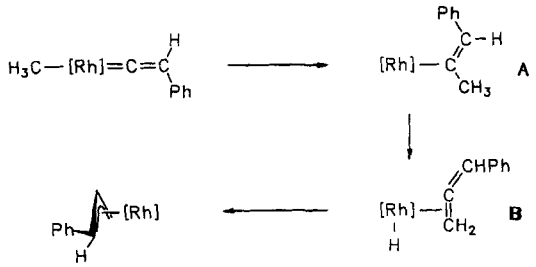
Scheme 9. L = P*i*Pr$_3$.



Scheme 11. L = P*i*Pr$_3$.

proton H2 and the terminal protonsH1, H3 and H4 (for exact assignment see Experimental Section) which are larger if H1, H3, or H4 is in an *anti* rather than in a *syn* position. Moreover, it is noteworthy that compound **41**, even after stirring for 24 h in benzene, does not rearrange to the *syn* isomer, which is supposed to be thermodynamically more stable.

With regard to the mechanism of the isomerization of the methyl(vinylidene) to the allyl complexes, in agreement with earlier studies,[20] we assume there is initial formation of an intermediate 14-electron species of composition **A** (Scheme 10),

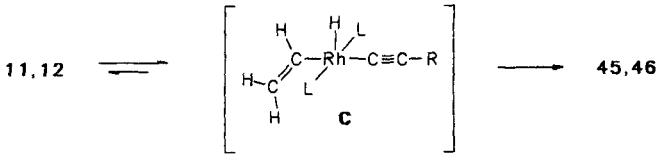


Scheme 10. [Rh] = Rh(P*i*Pr$_3$)$_2$.

which is analogous to [Rh(η^1-CH_2Ph)(P*i*Pr$_3$)$_2$].[18b] This intermediate then undergoes a β-H shift to give the four-coordinate (η^2-allene)hydridorhodium derivative **B**.[21] The final product is then generated by hydride transfer from the metal to the central carbon atom of the allene unit. Support for the assumption that a vinyl ligand such as in **A** can rearrange to a 1-substituted allyl group stems from previous work by Schwartz et al., who observed that the iridium compound *trans*-[Ir{(*Z*)-$C(CH_3)$=$CHCH_3$}(CO)(PPh_3)$_2$] reacts on warming in C_6D_6 to give the allyl isomer [Ir(η^3-*syn*-1-$CH_3C_3H_4$)(CO)(PPh_3)$_2$].[22] In the reaction of [$C_5H_5Mo(CH_3C{\equiv}CCH_3)LL'$]$BF_4$ (L = L′ = $P(OMe)_3$; L = CO, L′ = PEt_3) with hydride donors, a σ-vinyl intermediate is also formed which rearranges to the corresponding (η^3-1-methylallyl)molybdenum complex.[23]

The isomerization of the vinyl(vinylidene) compounds **11** and **12** in benzene proceeds more slowly and, after stirring for 3 h at 40–50 °C, affords the η^3-2,3,4-butadienyl derivatives **43** and **44** in 55–65% yield (Scheme 11). The ^{1}H NMR spectra (in C_6D_6) of the orange, very air-sensitive solids display complex patterns for the signals of protons H1–H4, which is due to Rh–H, P–H and H–H couplings. The resonances of the *syn* protons H3 reveal considerably smaller P–H coupling constants than those of the *anti* protons H4. This agrees with the spectroscopic data of **40–42**. In the ^{13}C NMR spectra of **43** and **44**, a significant difference in the chemical shift (ca. 100 ppm) for the signals of the carbon atoms C2 and C4 is observed (for assignment see Experimental Section). Therefore, we assume that the allylic fragment of the butadienyl unit is unsymmetrically coordinated to the metal center. This structural proposal is supported by the ^{31}P NMR spectra of **43** and **44**, which display two separate resonances (doublets of doublets) with significantly different Rh–P coupling constants. The difference $\Delta(\delta P)$ is much larger (32–36 ppm) than in the case of the allyl complexes **40** and **41** (5–8 ppm), for which an almost symmetrical type of bonding to rhodium can be assumed. The conclusion that the butadienyl derivatives are generated by an *intramolecular* route has been confirmed by a crossover experiment: upon stirring a solution of **12** and **18** in C_6D_6 for 1 h at 50 °C, only the corresponding isomers **40** and **44** are formed.

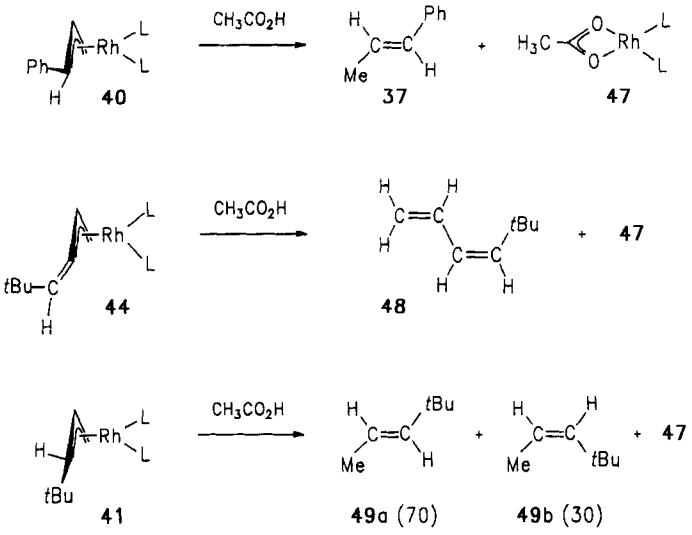
Most remarkably, the vinyl(vinylidene) complexes **11** and **12** are not only labile in solution, but also in the solid state. If they are stored under argon for 10–14 days at room temperature, the color changes from violet to brown without any sign of decomposition. Both the ^{1}H and ^{13}C NMR spectra of the brown products confirm that the alkynyl(ethene)rhodium(I) derivatives **45** and **46** (Scheme 11) were formed nearly quantitatively. They had previously been prepared from **1** and HC≡CR (R = Ph, *t*Bu) under an atmosphere of ethene.[8] With regard to the mechanism of the rearrangement of **11** and **12** to **45** and **46**, we assume that, in analogy to the formation of **23–25** from **8**, **10–13** (see Scheme 5), the initial step involves a 1,3-H shift from the vinylidene β-carbon atom to the metal. The five-coordinate intermediate **C** (Scheme 12) can then either regenerate the starting material **11**, **12** or react by intramolecular reductive coupling to give the ethene complexes **45** and **46**, respectively. In this context we note that a rearrangement of the alkynyl(hydrido)rhodium(III) compounds [RhH(C≡$CSiR_3$)-



Scheme 12. L = P*i*Pr$_3$.

$Cl(PiPr_3)_2$] (R = Me, Ph) to the vinylidene complexes *trans*-[RhCl(=C=CHSiR$_3$)($PiPr_3$)$_2$] has been observed to occur in the solid state. This is a 1,3-H shift in the reverse direction from the metal to the alkynyl β-carbon atom.[24]

The η^3-allyl and η^3-butadienylrhodium(I) compounds also react with acetic acid. It has already been mentioned (see Scheme 8) that on treatment of the η^1-vinyl complex **31** with CH_3CO_2H, (*E*)-2-methylstyrene is formed. This olefin is also obtained almost quantitatively upon acid-induced Rh–C bond cleavage from **40** and acetic acid in benzene at room temperature (Scheme 13). The corresponding reaction of **44** with

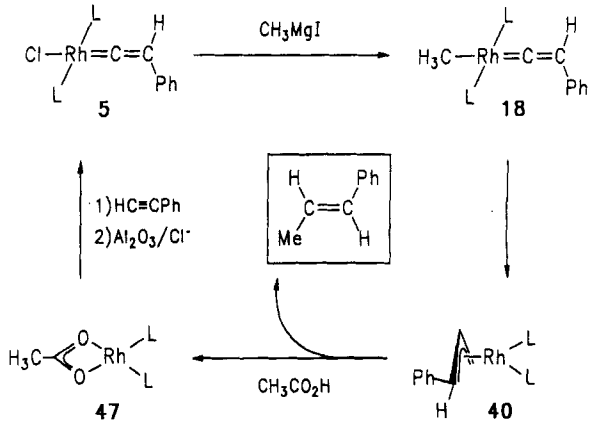


Scheme 13. L = $PiPr_3$.

CH_3CO_2H affords regioselectively the butadiene derivative **48**.[25] The exclusive formation of the *Z* isomer supports the assumption that in compound **44** (and probably also in **43**) the substituents at the non-coordinated double bond are *cis* disposed.

In contrast to **40**, the related *tert*-butylallyl complex **41** unexpectedly reacts with acetic acid to give a mixture of the *E* and *Z* isomers **49a,b** with the former as the major species. Since we failed to detect an intermediate in this process by NMR spectroscopy, we can only speculate about the reason for the different course of the reactions of **40** and **41** with CH_3CO_2H. From previous studies into the reactivity of [Rh(η^3-2-MeC_3H_4)-($PiPr_3$)$_2$] towards CF_3CO_2H we know that at low temperature an oxidative addition occurs and the π-allyl(hydrido)-rhodium(III) complex [RhH(η^3-2-MeC_3H_4)(η^1-O_2CCF_3)-($PiPr_3$)$_2$] is formed.[18b] If a structurally related species is generated on treatment of **40** or **41** with acetic acid as an intermediate, it could rearrange to an isomeric σ-allyl(hydrido) derivative, which would give **47** and CH_3CH=CHR by reductive elimination. Depending on whether steric or electronic effects determine the site of attack of the metal-bound proton on the allylic ligand, the *E* or the *Z* olefin could be formed, as has been observed in the reaction of **41** with CH_3CO_2H.

The rhodium-containing product of the reaction of **40**, **41** or **44** with acetic acid is the chelate complex **47**,[18b] which can be reconverted to the starting material **5**. This takes place in two steps, first by treatment of **47** with phenylacetylene, and second by column chromatography of the rhodium(III) compound [RhH(C≡CPh)(η^2-O_2CCH_3)($PiPr_3$)$_2$][26] (generated in situ) on Al_2O_3 in the presence of chloride ions. Therefore, a cyclic process (Scheme 14) can be established, in which an olefin



Scheme 14. L = $PiPr_3$.

RCH=CHR′ is regio- and eventually stereoselectively formed from a terminal alkyne HC≡CR, a Grignard reagent R′MgX, acetic acid, and general assistance from rhodium(I). Most recently, it was shown that not only olefins and butadienes, but also vinylallenes can be prepared by an analogous route, provided that instead of **5** the related allenylidene complex *trans*-[RhCl(=C=C=CPh_2)($PiPr_3$)$_2$] is used as the starting material.[27]

Conclusion

The present investigations have shown that a stereoselective coupling of an alkyl, aryl, or vinyl group with a vinylidene unit can occur within the coordination sphere of rhodium(I). This migratory insertion process may be considered as a counterpart to the coupling of a hydrocarbyl moiety with a carbene ligand, of which several examples are known.[28] The closest analogy to the synthesis of compounds **27**–**35** which we were aware of is the reaction of the iridium(III) vinylidene [$IrCH_3$(=C=CH_2)I{η^3-N($SiMe_2CH_2PPh_2$)$_2$}] with acetonitrile, which affords the vinyl complex [Ir{C(CH_3)=CH_2)(NCCH_3)I-{η^3-N($SiMe_2CH_2PPh_2$)$_2$}] in modest yield.[3d] Recently, Proulx and Bergman described a reaction of [(C_5H_5)$_2$Ta(=CH_2)CH_3] and [Re(R)(CO)$_5$] (R = Me, Ph) that gave a dinuclear complex containing alkenyl and oxotantalum groups bound to a rhenium center.[29] They assumed that a methyl- or phenyl(vinylidene)rhenium compound is involved as an intermediate, which, by migratory insertion, would form the alkenyl ligand.

The most remarkable feature of this work, however, is the coupling of the C-bonded ligands of the rhodium complexes **11**, **12** and **18**–**20**, which occurs *without* the presence of a supporting Lewis base. In order to explain the formation of a η^1-butadienyliridium(III) compound stabilized by an agostic C–H–Ir interaction, Selnau and Merola postulated that a vinyl-to-vinylidene migration takes place via an intermediate having the

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C-bonded ligands in adjacent positions.[3c] Although in **11**, **12**, and **18–20** the σ-bonded alkyl, aryl, or vinyl group and the vinylidene unit are definitely *trans* to each other, a migratory insertion can also occur which opens up a novel synthetic route to π-allyl- and π-butadienylrhodium complexes. That this type of intramolecular C–C coupling is not restricted to rhodium has recently been shown by the preparation of the ruthenium compound $[C_5H_5Ru\{\eta^3\text{-}2,3,4\text{-}CH_2CHC{=}CHCO_2Me\}(PPh_3)]$, which is obtained from $[C_5H_5RuCl(=C{=}CHCO_2Me)(PPh_3)]$ and $Sn(CH{=}CH_2)_4$ in the presence of CuCl in 70% yield.[30]

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk tube techniques. The starting material **15** was prepared as described in the literature [7]. NMR spectra were recorded at room temperature on Bruker AC200 and Bruker AMX400 instruments, IR spectra on a Perkin Elmer 1420 infrared spectrometer, and mass spectra on a Varian CH7 MAT or on a Finnigan 90 MAT instrument. Melting points were measured by DTA. Abbreviations used: s, singlet; d, doublet; t, triplet; vt, virtual triplet; m, multiplet; br, broadened signal.

Modified procedure for the preparation of *trans*-[RhCl(=C=CHPh)(P*i*Pr$_3$)$_2$] (5): A solution of $[RhCl(PiPr_3)_2]_2$ (500 mg, 0.55 mmol) in pentane (20 mL) was treated at −10 °C with phenylacetylene (240 μL, 1.10 mmol); this led to a rapid change of color from red to yellow. After the solvent was removed in vacuo, the residue was dissolved in NEt_3/benzene (5 mL; 1:1), and the solution stirred for 20 h at room temperature. A smooth change of color from yellow to dark blue occurred. The solvent was removed and the residue dissolved in acetone (10 mL). After the solution had been stored for 12 h at −78 °C, dark blue crystals precipitated, which were separated from the mother liquor, washed three times with 2 mL portions of acetone (−20 °C) and dried; yield 561 mg (92%). The compound was characterized by ^{1}H and ^{13}C NMR spectroscopy [4a].

***trans*-[RhCl(=C=CH*t*Bu)(P*i*Pr$_3$)$_2$] (6)**: A similar procedure was applied for the preparation of **6**, from $[RhCl(PiPr_3)_2]_2$ (250 mg, 0.27 mmol) and HC≡C*t*Bu (69 μL, 0.50 mmol) as starting materials. Dark blue crystalline solid; yield 274 mg (93%). The compound was characterized by ^{1}H and ^{13}C NMR spectroscopy [4b].

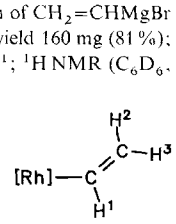
Modified procedure for the preparation of *trans*-[RhCl(=C=CH$_2$)(P*i*Pr$_3$)$_2$] (7): A slow stream of acetylene was passed through a solution of $[RhCl(PiPr_3)_2]_2$ in pentane at −10 °C until a change of color from red to yellow had occurred. The solution was worked up as described for **5** to give dark blue crystals; yield 223 mg (88%). The compound was characterized by ^{1}H and ^{13}C NMR spectroscopy [4a].

***trans*-[Rh(Ph)(=C=CHPh)(P*i*Pr$_3$)$_2$] (8)**: A solution of **5** (180 mg, 0.32 mmol) in ether (3 mL) was treated at −30 °C with a solution of C_6H_5MgBr in ether (0.33 mL, 1.0 M). After the reaction mixture had been warmed to room temperature, it was stirred for 1 h, and the solvent removed. The residue was extracted with pentane (30 mL), the extract concentrated to about 5 mL in vacuo, and then the solution was stored for 15 h at −78 °C. Violet crystals precipitated, which were separated from the mother liquor, washed three times with 2 mL portions of acetone (0 °C), and dried; yield 153 mg (79%); m.p. 110 °C (decomp.); IR (C_6H_6): $\tilde{\nu}$ = 1585, 1560 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.50 (m, 4H, *o*-C_6H_5), 7.14 (m, 6H, *m*-, *p*-C_6H_5), 2.28 (m, 6H, PC*H*CH$_3$), 1.16 [dvt, *N* = 13.1, *J*(H,H) = 7.1 Hz, 36H, PCHC*H*$_3$], signal of =C*H*Ph proton probably covered by signal of PC*H*CH$_3$; ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 296.7 [dt, *J*(Rh,C) = 47.0, *J*(P,C) = 17.8 Hz, Rh=*C*=CHR], 170.2 [dt, *J*(Rh,C) = 30.0, *J*(P,C) = 11.4 Hz, Rh-*ipso*-C_6H_5], 138.1 [t, *J*(P,C) = 2.5 Hz, C_6H_5], 129.0 (s, C_6H_5), 128.3, 126.2, 125.5, 124.2, 121.8 (all s, C_6H_5), 117.7 [dt, *J*(Rh,C) = 10.2, *J*(P,C) = 5.1 Hz, Rh=C=*C*HR], 25.8 (vt, *N* = 19.1 Hz, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 40.4 [d, *J*(Rh,P) = 146.2 Hz]; $C_{32}H_{53}P_2Rh$ (602.6): calcd C 63.78, H 8.86; found C 63.91, H 9.32.

***trans*-[Rh(4-C$_6$H$_4$Me)(=C=CHPh)(P*i*Pr$_3$)$_2$] (9)**: This was prepared as described for **8**, from **5** (228 mg, 0.41 mmol) and a solution of (4-C_6H_4Me)MgBr in ether (1.27 mL, 0.48 M). Violet microcrystalline solid; yield 176 mg (61%); m.p. 94–95 °C (decomp.); IR (C_6H_6): $\tilde{\nu}$ = 1590, 1565 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.13 (m, 9H, C_6H_4 and C_6H_5), 2.30 (m, 6H, PC*H*CH$_3$), 2.27 (s, 3H, $C_6H_4CH_3$), 1.17 [dvt, *N* = 13.2, *J*(H,H) = 7.3 Hz, 36H, PCHC*H*$_3$], signal of =C*H*Ph proton probably covered by signal of PC*H*CH$_3$; ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 296.4 [dt, *J*(Rh,C) = 47.0, *J*(P,C) = 17.8 Hz, Rh=*C*=CHPh], 164.9 [dt, *J*(Rh,C) = 27.0, *J*(P,C) = 12.3 Hz, Rh-*ipso*-$C_6H_4CH_3$], 137.8 [t, *J*(P,C) = 2.8 Hz, C_6H_4R], 130.1 (s, C_6H_4R), 128.8 [t, *J*(P,C) = 2.6 Hz, C_6H_4R], 128.4, 127.1, 125.4, 124.0 (all s, C_6H_4R), 117.7 [dt, *J*(Rh,C) = 10.2, *J*(P,C) = 5.1 Hz, Rh=C=*C*HPh], 25.7 (vt, *N* = 17.8 Hz, P*C*HCH$_3$), 21.3 (s, $C_6H_4CH_3$), 20.2 (s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 40.6 [d, *J*(Rh,P) = 145.6 Hz]; $C_{33}H_{55}P_2Rh$ (616.7): calcd C 64.28, H 8.99; found C 63.93, H 9.36.

***trans*-[Rh(Ph)(=C=CH*t*Bu)(P*i*Pr$_3$)$_2$] (10)**: To a solid sample of PhMgBr, which was obtained after removing the solvent from a solution of PhMgBr in ether (0.35 mL, 1.0 M), a solution of **6** (150 mg, 0.28 mmol) in toluene (3 mL) was slowly added at −30 °C. After the reaction mixture had been warmed to room temperature, it was stirred for 1 h, and then the solvent was removed. The residue was extracted with pentane (30 mL), the extract filtered, and the filtrate was brought to dryness in vacuo. The residue was dissolved in acetone (3 mL), and the solution stored for 15 h at −78 °C. Violet crystals precipitated which were isolated as described for **8**; yield 137 mg (85%); m.p. 73 °C (decomp.); IR (C_6H_6): $\tilde{\nu}$ = 1610, 1555 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.44 (m, 2H, *o*-C_6H_5), 7.16 (m, 2H, *m*-C_6H_5), 6.96 (m, 1H, *p*-C_6H_5), 2.44 (m, 6H, PC*H*CH$_3$), 1.23 [dvt, *N* = 13.0, *J*(H,H) = 7.1 Hz, 36H, PCHC*H*$_3$], 1.12 [s, 9H, C(CH$_3$)$_3$], 0.59 [t, *J*(P,H) = 4.4 Hz, 1H, =C*H*R]; ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 291.1 [dt, *J*(Rh,C) = 46.4, *J*(P,C) = 16.5 Hz, Rh=*C*=CHR], 179.1 [dt, *J*(Rh,C) = 30.0, *J*(P,C) = 12.1 Hz, Rh-*ipso*-C_6H_5], 138.3 [t, *J*(P,C) = 2.2 Hz, C_6H_5], 125.9, 121.4 (both s, C_6H_5), 123.0 [dt, *J*(Rh,C) = 10.2, *J*(P,C) = 5.1 Hz, Rh=C=*C*HR], 32.2 [s, *C*(CH$_3$)$_3$], 27.1 [t, *J*(P,C) = 1.9 Hz, C(*C*H$_3$)$_3$], 25.8 [dvt, *J*(Rh,C) = 1.3, *N* = 19.1 Hz, P*C*HCH$_3$], 20.3 (s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 38.9 [d, *J*(Rh,P) = 147.9 Hz]; $C_{30}H_{57}P_2Rh$ (582.6): C 61.85, H 9.86; found C 61.94, H 10.02.

***trans*-[Rh(CH=CH$_2$)(=C=CHPh)(P*i*Pr$_3$)$_2$] (11)**: This was prepared as described for **8**, from **5** (200 mg, 0.36 mmol) and a solution of CH_2=CHMgBr in THF (0.38 mL, 1.0 M). Violet microcrystalline solid; yield 160 mg (81%); m.p. 76 °C (decomp.); IR (C_6H_6): $\tilde{\nu}$ = 1580 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.88 [m, in ^{1}H{^{31}P} ddd, *J*(Rh,H-1) = 1.2, *J*(H-1,H-2) = 19.6, *J*(H-1,H-3) = 14.2 Hz, 1H, H-1], 7.29 (m, 2H, *o*-C_6H_5), 7.14 (m, 2H, *m*-C_6H_5), 6.88 (m, 1H, *p*-C_6H_5), 6.29 [m, in ^{1}H{^{31}P} ddd, *J*(Rh,H-3) = 3.0, *J*(H-1,H-3) = 14.2, *J*(H-2,H-3) = 4.4 Hz, 1H, H-3], 5.30 [m, in ^{1}H{^{31}P} ddd, *J*(Rh,H-2) = 1.3, *J*(H-1,H-2) = 19.6, *J*(H-2,H-3) = 4.4 Hz, 1H, H-2], 2.52 (m, 6H, PC*H*CH$_3$), 2.02 [t, *J*(P,H) = 3.7 Hz, 1H, =C*H*R], 1.27 [dvt, *N* = 13.2, *J*(H,H) = 7.1 Hz, 36H, PCHC*H*$_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 300.6 [dt, *J*(Rh,C) = 47.2, *J*(P,C) = 16.9 Hz, Rh=*C*=CHR], 173.6 [dt, *J*(Rh,C) = 26.5, *J*(P,C) = 13.6 Hz, Rh-*C*H=CH$_2$], 129.7, 128.8, 128.7, 126.4 (all s, C_6H_5), 120.7 [t, *J*(P,H) = 3.6 Hz, Rh-CH=*C*H$_2$], 118.0 [dt, *J*(Rh,C) = 10.4, *J*(P,C) = 5.5 Hz, Rh=C=*C*HR], 25.6 [dvt, *J*(Rh,C) = 1.2, *N* = 20.1 Hz, P*C*HCH$_3$], 20.5 (s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 43.8 [d, *J*(Rh,P) = 145.3 Hz]; $C_{28}H_{51}P_2Rh$ (552.6): calcd C 60.86, H 9.30; found C 60.56, H 9.60.



***trans*-[Rh(CH=CH$_2$)(=C=CH*t*Bu)(P*i*Pr$_3$)$_2$] (12)**: This was prepared as described for **8**, from **6** (135 mg, 0.25 mmol) in toluene (3 mL) and a solution of CH_2=CHMgBr in THF (0.40 mL, 1.0 M). Violet microcrystalline solid; yield 101 mg (76%); m.p. 63 °C (decomp.); IR (C_6H_6): $\tilde{\nu}$ = 1590 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.97 [m, in ^{1}H{^{31}P} dd, *J*(H-1,H-2) = 19.7, *J*(H-1,H-3) = 14.4 Hz, 1H, H-1], 6.28 [m, in ^{1}H{^{31}P} ddd, *J*(Rh,H-3) = 1.2, *J*(H-1,H-3) = 14.4, *J*(H-2,H-3) = 4.2 Hz, 1H, H-3], 5.30 [m, in ^{1}H{^{31}P} ddd, *J*(Rh,H-2) = 1.3, *J*(H-1,H-2) = 19.7, *J*(H-2,H-3) = 4.2 Hz, 1H, H-2], 2.71 (m, 6H, PC*H*CH$_3$), 1.34 [dvt, *N* = 12.9, *J*(H,H) = 7.1 Hz, 36H, PCHC*H*$_3$], 1.07 [s, 9H, C(CH$_3$)$_3$], 0.27 [t, *J*(P,H) = 3.9 Hz, 1H, =CHR], for assignment of H-1, H-2 and H-3 see **11**; ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 297.7 [dt, *J*(Rh,C) = 46.4, *J*(P,C) = 17.2 Hz, Rh=*C*=CHR],

175.5 [dt, J(Rh,C) = 26.7, J(P,C) = 13.7 Hz, Rh–*C*H=CH_2], 123.6 [dt, J(Rh,C) = 10.2, J(P,C) = 5.1 Hz, Rh=C=*C*HR], 119.8 [t, J(P,C) = 3.5 Hz, Rh–CH=*C*H_2], 32.3 [s, C(CH_3)$_3$], 31.3 [s, *C*(CH_3)$_3$], 25.5 [dvt, J(Rh,C) = 1.9, N = 19.1 Hz, P*C*HCH_3], 20.5 (s, PCH*C*H_3); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 41.7 [d, J(Rh,P) = 147.3 Hz]; $C_{26}H_{55}P_2Rh$ (532.6): calcd C 58.64, H 10.41; found C 58.46, H 10.51.

***trans*-[Rh(CH=CH_2)(=C=CH_2)(P*i*Pr$_3$)$_2$] (13)**: A solution of **7** (140 mg, 0.29 mmol) in benzene (5 mL) was treated with a solution of CH_2=CHMgBr in THF (0.5 mL, 1.0 M) and stirred for 1 h at room temperature. After the solvent had been removed, the residue was extracted with pentane (20 mL), the extract then filtered, and the filtrate was brought to dryness in vacuo. The residue was recrystallized from acetone (3 mL) to give, after the solution had been stored for 12 h at −20 °C, dark green crystals; yield 109 mg (79%); m.p. 83 °C (decomp.); IR (C_6H_6): $\tilde{\nu}$ = 1600 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.76 (m, 1H, H-1), 6.20 (m, 1H, H-3), 5.30 (m, 1H, H-2), 2.68 (m, 6H, PC*H*CH_3), 1.30 [dvt, N = 13.1, J(H,H) = 7.1 Hz, 36H, PCHC*H*$_3$], −0.01 (m, 2H, =CH_2), for assignment of H-1, H-2 and H-3 see **11**; ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 303.9 [dt, J(Rh,C) = 45.8, J(P,C) = 16.5 Hz, Rh=*C*=CH_2], 176.5 [dt, J(Rh,C) = 25.4, J(P,C) = 10.8 Hz, Rh–*C*H=CH_2], 120.8 [t, J(P,C) = 3.5 Hz, Rh–CH=*C*H_2], 94.9 [dt, J(Rh,C) = 11.4, J(P,C) = 5.1 Hz, Rh=C=*C*H_2], 25.0 [dvt, J(Rh,C) = 1.3, N = 19.7 Hz, P*C*HCH_3], 20.4 (s, PCH*C*H_3); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 43.7 [d, J(Rh,P) = 147.0 Hz]; $C_{22}H_{47}P_2Rh$ (476.5): calcd C 55.46, H 9.94; found C 55.66, H 10.29.

***trans*-[Rh(CH=CMe_2)(=C=CHPh)(P*i*Pr$_3$)$_2$] (14)**: This was prepared as described for **8**, from **5** (100 mg, 0.18 mmol) and a solution of Me_2C=CHMgBr in THF (0.50 mL, 1.0 M). Violet microcrystalline solid; yield 80 mg (77%); m.p. 81 °C (decomp.); IR (C_6H_6): $\tilde{\nu}$ = 1580, 1560 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.29 (m, 2H, *o*-C_6H_5), 7.16 (m, 2H, *m*-C_6H_5), 6.87 (m, 1H, *p*-C_6H_5), 6.13 (m, 1H, Rh–CH=CMe_2), 2.35 (m, 6H, PC*H*CH_3), 2.17 [dt, J(P,H) = 4.2, J(Rh,H) = 4.0 Hz, 1H, =C*H*R], 2.04 [m, 6H, =C(CH_3)$_2$], 1.27 [dvt, N = 13.1, J(H,H) = 6.9 Hz, 36H, PCHC*H*$_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 296.2 [dt, J(Rh,C) = 46.4, J(P,C) = 17.2 Hz, Rh=*C*=CHR], 152.8 [dt, J(Rh,C) = 27.3, J(P,C) = 13.4 Hz, Rh–*C*H=CMe$_2$], 131.5 [t, J(P,H) = 3.8 Hz, Rh–CH=*C*Me$_2$], 128.8 (brs, *ipso*-C_6H_5), 128.4, 125.3, 123.8 (all s, C_6H_5), 117.5 [dt, J(Rh,C) = 10.2, J(P,C) = 5.7 Hz, Rh=C=*C*HR], 30.3 [m, =C(*C*H_3)$_2$], 26.0 [dvt, J(Rh,C) = 1.3, N = 19.7 Hz, P*C*HCH_3], 20.4 (s, PCH*C*H_3); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 43.1 [d, J(Rh,P) = 146.0 Hz]; $C_{30}H_{55}P_2Rh$ (580.6): calcd C 62.06, H 9.55, Rh 17.79; found C 62.21, H 9.87, Rh 17.54.

***trans*-[Rh(Ph)(=C=CMe_2)(P*i*Pr$_3$)$_2$] (16)**: A solution of **15** (85 mg, 0.17 mmol) in toluene (2 mL) was treated at −30 °C with a solution of PhMgBr in ether (0.30 mL, 1.5 M). After the reaction mixture had been warmed to room temperature, it was stirred for 3 h, and the solvent removed. The residue was extracted with pentane (30 mL), the extract was brought to dryness in vacuo, and the residue recrystallized from acetone (2 mL). After the solution had been stored for 15 h at −78 °C, violet crystals precipitated; yield 75 mg (81%); m.p. 75 °C (decomp.); IR (C_6H_6): $\tilde{\nu}$ = 1660, 1550 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.46 (m, 2H, *o*-C_6H_5), 7.19 (m, 2H, *m*-C_6H_5), 6.98 (m, 1H, *p*-C_6H_5), 2.24 (m, 6H, PC*H*CH_3), 1.83 [t, J(P,H) = 2.4 Hz, 6H, =C(CH_3)$_2$], 1.20 [dvt, N = 12.9, J(H,H) = 7.1 Hz, 36H, PCHC*H*$_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 294.7 [dt, J(Rh,C) = 44.5, J(P,C) = 18.4 Hz, Rh=*C*=CMe$_2$], 172.8 [dt, J(Rh,C) = 28.0, J(P,C) = 12.7 Hz, Rh–*ipso*-C_6H_5], 138.5 [t, J(P,C) = 1.9 Hz, C_6H_5], 125.8, 121.3 (all s, C_6H_5), 110.7 [dt, J(Rh,C) = 10.2, J(P,C) = 5.7 Hz, Rh=C=*C*Me$_2$], 25.4 [dvt, J(Rh,C) = 1.3, N = 19.1 Hz, P*C*HCH_3], 20.3 (s, PCH*C*H_3), 8.25 [t, J(P,C) = 2.5 Hz, =C(CH_3)$_2$]; ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 41.2 [d, J(Rh,P) = 147.0 Hz]; $C_{28}H_{53}P_2Rh$ (554.6): calcd C 60.64, H 9.63; found C 59.76, H 10.35.

***trans*-[Rh(CH=CH_2)(=C=CMe_2)(P*i*Pr$_3$)$_2$] (17)**: This was prepared as described for **8**, from **15** (120 mg, 0.23 mmol) in toluene (3 mL) and a solution of CH_2=CHMgBr in THF (5.5 mL, 1.0 M). Dark green crystals; yield 94 mg (80%); m.p. 75 °C (decomp.); IR (C_6H_6): $\tilde{\nu}$ = 1665 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.90 [dddt, J(P,H-1) = 2.9, J(Rh,H-1) = 0.6, J(H-1,H-2) = 19.9, J(H-1,H-3) = 14.8 Hz, 1H, H-1], 6.30 [m, in ^{1}H{^{31}P} ddd, J(Rh,H-3) = 2.7, J(H-1,H-3) = 14.8, J(H-2,H-3) = 4.7 Hz, 1H, H-3], 5.30 [m, in ^{1}H{^{31}P} ddd, J(Rh,H-2) = 1.4, J(H-1,H-2) = 19.9, J(H-2,H-3) = 4.7 Hz, 1H, H-2], 2.53 (m, 6H, PC*H*CH_3), 1.76 [t, J(P,H) = 2.4 Hz, 6H, =C(CH_3)$_2$], 1.31 [dvt, N = 13.0, J(H,H) = 7.2 Hz, 36H, PCHCH_3], for assignment of H-1, H-2 and H-3 see **11**; ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 298.1 [dt, J(Rh,C) = 44.4, J(P,C) = 18.3 Hz, Rh=*C*=CMe$_2$], 176.6 [dt, J(Rh,C) = 26.4, J(P,C) = 13.0 Hz, Rh–*C*H=CH_2], 120.4 (brs, Rh–CH=*C*H_2), 110.6 [dt, J(Rh,C) = 10.6, J(P,C) = 5.8 Hz, Rh=C=*C*Me$_2$], 25.1 (vt, N = 18.8 Hz, P*C*HCH_3), 20.5 (s, PCH*C*H_3), 7.4 [s, =C(*C*H_3)$_2$]; ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 44.4 [d, J(Rh,P) = 147.6 Hz]; $C_{24}H_{51}P_2Rh$ (504.5): calcd C 57.14, H 10.19; found C 57.63, H 9.75.

***trans*-[Rh(Me)(=C=CHPh)(P*i*Pr$_3$)$_2$] (18)**: To a solid sample of MeMgI, which was obtained after removing the solvent from a solution of MeMgI in ether (0.35 mL, 1.0 M), a solution of **5** (180 mg, 0.32 mmol) in toluene (3 mL) was slowly added at −30 °C. The reaction mixture was stirred for 5 min at −30 °C, and the solvent removed. The residue was worked up as described for **8**. Violet microcrystalline solid; yield 151 mg (87%); m.p. 75 °C (decomp.); IR (C_6H_6): $\tilde{\nu}$ = 1590 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.30 (m, 2H, *o*-C_6H_5), 7.14 (m, 2H, *m*-C_6H_5), 6.88 (m, 1H, *p*-C_6H_5), 2.28 (m, 6H, PC*H*CH_3), 1.70 [t, J(P,H) = 3.7 Hz, 1H, =C*H*R], 1.26 [dvt, N = 13.0, J(H,H) = 6.9 Hz, 36H, PCHC*H*$_3$], −0.08 [brt, J(P,H) = 5.8 Hz, 3H, Rh–CH_3]; ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 294.9 [dt, J(Rh,C) = 47.9, J(P,C) = 16.8 Hz, Rh=*C*=CHR], 129.5, 128.3, 125.2, 123.9 (all s, C_6H_5), 116.5 [dt, J(Rh,C) = 10.7, J(P,C) = 4.5 Hz, Rh=C=*C*HR], 25.2 [dvt, J(Rh,C) = 1.2, N = 18.9 Hz, P*C*HCH_3], 20.2 (s, PCH*C*H_3), −1.7 [dt, J(Rh,C) = 19.2, J(P,C) = 11.6 Hz, Rh–CH_3]; ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 45.8 [d, J(Rh,P) = 146.8 Hz]; $C_{27}H_{51}P_2Rh$ (540.6): calcd C 59.99, H 9.51; found C 59.46, H 9.99.

***trans*-[Rh(Me)(=C=CH*t*Bu)(P*i*Pr$_3$)$_2$] (19)**: This was prepared as described for **18**, from solid MeMgI (0.35 mmol) and **6** (95 mg, 0.18 mmol) as starting materials. Dark violet crystals; yield 74 mg (81%); m.p. 82 °C (decomp.); IR (C_6H_6): $\tilde{\nu}$ = 1640 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): δ = 2.68 (m, 6H, PC*H*CH_3), 1.32 [dvt, N = 12.8, J(H,H) = 7.1 Hz, 36H, PCHC*H*$_3$], 1.07 [s, 9H, C(CH_3)$_3$], −0.16 [brt, J(P,H) = 5.7 Hz, 3H, Rh–CH_3], signal of =C*H*tBu covered by signal of Rh–CH_3; ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 44.5 [d, J(Rh,P) = 148.1 Hz]; $C_{25}H_{55}P_2Rh$ (520.6): calcd C 57.68, H 10.65; found C 57.31, H 10.39.

***trans*-[Rh(Me)(=C=CH_2)(P*i*Pr$_3$)$_2$] (20)**: This was prepared as described for **18**, from solid MeMgI (0.35 mmol) and **7** (87 mg, 0.18 mmol) as starting materials. Black microcrystalline solid; yield 66 mg (79%); m.p. 92 °C (decomp.); IR (C_6H_6): $\tilde{\nu}$ = 1605 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): δ = 2.70 (m, 6H, PC*H*CH_3), 1.31 [dvt, N = 13.0, J(H,H) = 7.1 Hz, 36H, PCHC*H*$_3$], −0.29 (m, 5H, Rh–CH_3 and =CH_2); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 45.9 [d, J(Rh,P) = 148.2 Hz]; $C_{21}H_{47}P_2Rh$ (464.5): calcd C 54.31, H 10.20; found C 53.81, H 9.79.

***trans*-[Rh(C≡CPh)(=C=CHPh)(P*i*Pr$_3$)$_2$] (21)**: A solution of **5** (100 mg, 0.18 mmol) in ether (4 mL) was treated at −30 °C with a solution of PhC≡CMgBr in THF (0.50 mL, 1.0 M). After the reaction mixture had been warmed to room temperature, it was stirred for 2 h and then worked up as described for **10**. Violet crystals; yield 87 mg (78%). The compound was characterized by IR, ^{1}H and ^{13}C NMR spectroscopy [1,8b].

***trans*-[Rh(C≡CPh)(=C=CH*t*Bu)(P*i*Pr$_3$)$_2$] (22)**: This was prepared as described for **21**, from **6** (210 mg, 0.39 mmol) and a solution of PhC≡CMgBr in THF (0.80 mL, 1.0 M). Green crystals; yield 186 mg (79%); m.p. 97 °C (decomp.); IR (C_6H_6): $\tilde{\nu}$ = 2060 (C≡C), 1660, 1630, 1590 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.38 (m, 2H, *o*-C_6H_5), 7.11 (m, 2H, *m*-C_6H_5), 6.91 (m, 1H, *p*-C_6H_5), 2.86 (m, 6H, PC*H*CH_3), 1.39 [dvt, N = 13.1, J(H,H) = 6.9 Hz, 36H, PCHC*H*$_3$], 1.05 [s, 9H, C(CH_3)$_3$], −0.06 [t, J(P,H) = 3.7 Hz, 1H, =C*H*R]; ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 308.2 [dt, J(Rh,C) = 49.0, J(P,C) = 15.9 Hz, Rh=*C*=CHR], 136.2 [dt, J(Rh,C) = 9.5, J(P,C) = 1.9 Hz, Rh–C≡*C*R], 130.1, 128.3, 125.0 (all s, C_6H_5), 121.2 [dt, J(Rh,C) = 12.7, J(P,C) = 5.1 Hz, Rh=C=*C*HR], 32.3 [s, *C*(CH_3)$_3$], 30.1 [s,*C*(CH_3)$_3$], 25.4 [dvt, J(Rh,C) = 1.3, N = 20.3 Hz, P*C*HCH_3], 20.7 (s, PCH*C*H_3), signal of Rh–*C*≡CR probably covered by signal of C_6H_6; ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 46.5 [d, J(Rh,P) = 136.4 Hz]; $C_{32}H_{57}P_2Rh$ (606.7): calcd C 63.36, H 9.47, Rh 16.96; found C 62.94, H 9.42, Rh 16.73.

Preparation of *trans*-[Rh(C≡CR)(py)(P*i*Pr$_3$)$_2$] (23–25) from *trans*-[Rh(R')(=C=CHR)(P*i*Pr$_3$)$_2$] (8, 10–13): A solution of **8**, **10**, **11**, **12**, or **13**

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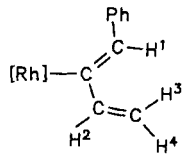
(0.10 mmol) in ether (2 mL) was treated with pyridine (100 μL, 1.25 mmol) and stirred for 30 min at room temperature. A change of color from violet to orange occurred. The solvent was removed and the orange residue was identified by IR and NMR spectroscopy as **23–25** [6,8b]. Yield quantitative. In addition to the proton signals of **23** a further singlet was observed at $\delta = 5.28$, assigned to ethene, if the reaction of **11** with pyridine was carried out in a NMR tube (in C_6D_6).

***trans*-[Rh{η^1-(*Z*)-C(Ph)=CHPh}(CO)(P*i*Pr$_3$)$_2$] (27)**: A stream of CO was passed through a solution of **8** (115 mg, 0.19 mmol) in toluene (3 mL) for 10 s at −30 °C. After the solution had been stirred for 2–3 min at −30 °C, it was warmed to room temperature, and the solvent removed. The residue was dissolved in acetone (2 mL), and the solution stored for 24 h at −30 °C. Yellow crystals precipitated, which were separated from the mother liquor, washed three times with 2 mL portions of acetone (0 °C), and dried; yield 112 mg (93%); m.p. 106 °C (decomp.); MS (70 eV): *m/z* 630 (M^+); IR (KBr): $\tilde{\nu} = 1930$ (C≡O) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 8.57$ (brs, 2H, =CH-*o*-C_6H_5), 7.81 (m, 2H, *o*-C_6H_5), 7.64 [dt, J(Rh,H) = 2.0, J(P,H) = 2.0 Hz, 1H, =C*H*R], 7.17 (m, 6H, *m*-, *p*-C_6H_5 and *m*-, *p*-=CH-C_6H_5), 2.25 (m, 6H, PC*H*CH$_3$), 1.13 [dvt, $N = 13.8$, J(H,H) = 6.9 Hz, 18H, PCHC*H*$_3$], 1.09 [dvt, $N = 13.8$, J(H,H) = 6.9 Hz, 18H, PCHC*H*$_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 195.5$ [dt, J(Rh,C) = 54.7, J(P,C) = 15.9 Hz, Rh-CO], 181.4 [dt, J(Rh,C) = 29.4, J(P,C) = 14.0 Hz, Rh-*C*(R)=CHR], 154.2 [t, J(P,C) = 1.9 Hz, *ipso*-C_6H_5], 144.6 [dt, J(Rh,C) = 1.9, J(P,C) = 1.3 Hz, *ipso*-C_6H_5], 137.3 [t, J(P,C) = 4.5 Hz, Rh-C(R)=*C*HR], 130.2, 129.9, 127.7, 127.2, 125.0, 124.9 (all s, C_6H_5), 25.68 [dvt, J(Rh,C) = 1.2, $N = 19.1$ Hz, PCHCH$_3$], 20.47, 20.17 (both s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 40.0$ [d, J(Rh,P) = 140.2 Hz]; $C_{33}H_{53}OP_2Rh$ (630.6): calcd C 62.85, H 8.47; found C 62.59, H 8.72.

***trans*-[Rh{η^1-(*Z*)-C(4-C$_6$H$_4$Me)=CHPh}(CO)(P*i*Pr$_3$)$_2$] (28)**: This was prepared as described for **27**, from **9** (120 mg, 0.19 mmol) and CO as starting materials. Yellow microcrystalline solid; yield 114 mg (91%); m.p. 146 °C (decomp.); IR (KBr): $\tilde{\nu} = 1930$ (C≡O) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 8.56$ (brs, 2H, *o*-C_6H_5), 7.76 (m, 2H, *o*-$C_6H_4CH_3$), 7.66 [dt, J(Rh,H) = 2.0, J(P,H) = 1.9 Hz, 1H, Rh-C(R')=C*H*R], 7.17 (m, 5H, *m*-, *p*-C_6H_5 and *m*-C_6H_4Me), 2.25 (m, 6H, PC*H*CH$_3$), 2.20 (s, 3H, $C_6H_4CH_3$), 1.14 [dvt, $N = 13.7$, J(H,H) = 7.2 Hz, 18H, PCHC*H*$_3$], 1.10 [dvt, $N = 13.2$, J(H,H) = 7.0 Hz, 18H, PCHC*H*$_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 195.6$ [dt, J(Rh,C) = 54.5, J(P,C) = 15.9 Hz, Rh-CO], 181.2 [dt, J(Rh,C) = 29.1, J(P,C) = 14.0 Hz, Rh-*C*(R')=CHR], 151.3 [t, J(P,C) = 1.3 Hz, *ipso*-$C_6H_4CH_3$], 144.8 (brs, =CH-*ipso*-C_6H_5), 136.7 [t, J(P,C) = 3.9 Hz, Rh-C(R')=*C*HR], 134.2 (s, *p*-$C_6H_4CH_3$), 130.2, 129.8, 128.0, 127.7, 124.8 (all s, *o*-, *m*-, *p*-C_6H_5 and *o*-, *m*-, $C_6H_4CH_3$), 25.7 [dvt, J(Rh,C) = 1.4, $N = 19.4$ Hz, PCHCH$_3$], 20.6, 20.2 (both s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 40.0$ [d, J(Rh,P) = 141.0 Hz]; $C_{34}H_{55}OP_2Rh$ (644.7): calcd C 63.35, H 8.60; found C 63.23, H 8.79.

***trans*-[Rh{η^1-(*Z*)-C(Ph)=CH*t*Bu}(CO)(P*i*Pr$_3$)$_2$] (29)**: This was prepared as described for **27**, from **10** (80 mg, 0.14 mmol) and CO as starting materials. Yellow microcrystalline solid; yield 76 mg (91%); m.p. 89 °C (decomp.); IR (KBr): $\tilde{\nu} = 1930$ (C≡O) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 7.77$ (m, 2H, *o*-C_6H_5), 7.17 (m, 2H, *m*-C_6H_5), 7.02 (m, 1H, *p*-C_6H_5), 6.63 [dt, J(Rh,H) = 1.8, J(P,H) = 2.0 Hz, 1H, =C*H*R], 2.37 (m, 6H, PC*H*CH$_3$), 1.51 [s, 9H, C(CH$_3$)$_3$], 1.21 [dvt, $N = 13.0$, J(H,H) = 7.1 Hz, 18H, PCHC*H*$_3$], 1.20 [dvt, $N = 13.3$, J(H,H) = 6.9 Hz, 18H, PCHC*H*$_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 195.6$ [dt, J(Rh,C) = 54.3, J(P,C) = 16.9 Hz, Rh-CO], 162.6 [dt, J(Rh,C) = 30.3, J(P,C) = 13.4 Hz, Rh-*C*(R')=CHR], 155.5 [t, J(P,C) = 1.2 Hz, *ipso*-C_6H_5], 147.4 [t, J(P,C) = 3.9 Hz, Rh-C(R')=*C*HR], 130.6, 126.9, 124.2 (all s, C_6H_5), 35.12 [dt, J(Rh,C) = 1.2, J(P,C) = 1.2 Hz, *C*(CH$_3$)$_3$], 31.8 [t, J(P,C) = 1.6 Hz, C(*C*H$_3$)$_3$], 25.6 [dvt, J(Rh,C) = 1.4, $N = 18.5$ Hz, PCHCH$_3$], 20.6, 20.5 (both s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 38.4$ [d, J(Rh,P) = 142.9 Hz]; $C_{31}H_{57}OP_2Rh$ (610.7): calcd C 60.97, H 9.41; found C 60.66, H 9.46.

***trans*-[Rh{η^1-(*Z*)-C(CH=CH$_2$)=CHPh}(CO)(P*i*Pr$_3$)$_2$] (30)**: This was prepared as described for **27**, from **11** (90 mg, 0.16 mmol) and CO as starting materials. Yellow crystals; yield 87 mg (92%); m.p. 96 °C (decomp.); IR (KBr): $\tilde{\nu} = 1930$ (C≡O) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 8.51$ (brs, 2H, *o*-C_6H_5), 7.49 (m, 1H, H-1), 7.16 (m, 3H, *m*-, *p*-C_6H_5), 5.39 [dd, J(H-2,H-3) = 16.7, J(H-3,H-4) = 3.1 Hz, 1H, H-3], 4.88 [dd, J(H-2,H-4) = 10.0, J(H-3,H-4) = 3.1 Hz, 1H, H-4], 2.27 (m, 6H, PC*H*CH$_3$), 1.25 [dvt, $N = 13.7$, J(H,H) = 7.1 Hz, 18H, PCHC*H*$_3$], 1.07 [dvt, $N = 13.0$, J(H,H) = 7.0 Hz, 18H, PCHC*H*$_3$], signal of H-2 probably covered by one of the resonances of the aromatic protons; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 195.7$ [dt, J(Rh,C) = 54.0, J(P,C) = 15.2 Hz, Rh-CO], 181.6 [dt, J(Rh,C) = 28.2, J(P,C) = 13.9 Hz, Rh-*C*(CH=CH$_2$)], 152.7 [s, Rh-C(*C*H=CH$_2$)], 144.6 (s, *ipso*-C_6H_5), 136.5 [t, J(P,C) = 3.7 Hz, Rh-C(R)=*C*HPh], 130.1, 127.7, 124.9 (all s, C_6H_5), 108.6 [s, Rh-C(CH=*C*H$_2$)], 26.1 (vt, $N = 19.5$ Hz, PCHCH$_3$), 20.9, 19.9 (both s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 41.5$ [d, J(Rh,P) = 140.9 Hz]; $C_{29}H_{51}OP_2Rh$ (580.6): calcd C 60.00, H 8.85; found C 60.04, H 9.15.



***trans*-[Rh{η^1-(*Z*)-C(Me)=CHPh}(CO)(P*i*Pr$_3$)$_2$] (31)**: This was prepared as described for **27**, from **18** (95 mg, 0.18 mmol) and CO as starting materials. Yellow crystals; yield 86 mg (87%); m.p. 148 °C (decomp.); IR (KBr): $\tilde{\nu} = 1925$ (C≡O) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 8.50$ (brs, 2H, *o*-C_6H_5), 7.32 (m, 2H, *m*-C_6H_5), 7.22 (m, 1H, =C*H*R), 7.04 (m, 1H, *p*-C_6H_5), 2.40 [s, 3H, Rh-C(CH$_3$)], 2.18 (m, 6H, PC*H*CH$_3$), 1.26 [dvt, $N = 13.8$, J(H,H) = 7.1 Hz, 18H, PCHC*H*$_3$], 1.06 [dvt, $N = 13.0$, J(H,H) = 7.1 Hz, 18H, PCHC*H*$_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 195.9$ [dt, J(Rh,C) = 53.2, J(P,C) = 15.3 Hz, Rh-CO], 182.3 [dt, J(Rh,C) = 28.7, J(P,C) = 14.3 Hz, Rh-C(R')], 145.3 (s, *ipso*-C_6H_5), 135.6 [t, J(P,C) = 3.7 Hz, Rh-C(R')=CHR], 129.7, 127.7, 123.9 (all s, C_6H_5), 33.4 [dt, J(Rh,C) = 2.4, J(P,C) = 2.4 Hz, Rh-*C*(CH$_3$)], 26.6 [dvt, J(Rh,C) = 1.4, $N = 19.4$ Hz, PCHCH$_3$], 20.8, 19.8 (both s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 43.2$ [d, J(Rh,P) = 145.3 Hz]; $C_{28}H_{51}OP_2Rh$ (568.6): calcd C 59.15, H 9.04; found C 58.76, H 9.17.

***trans*-[Rh{η^1-(*Z*)-C(Ph)=CMe$_2$}(CO)(P*i*Pr$_3$)$_2$] (32)**: A stream of CO was passed through a solution of **16** (55 mg, 0.10 mmol) in toluene (3 mL) for 10 s at −100 °C. After the solution had been stirred for 5 min at −100 °C, it was worked up as described for **27**. Yellow microcrystalline solid; yield 39 mg (67%); m.p. 121 °C (decomp.); IR (KBr): $\tilde{\nu} = 1930$ (C≡O) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 7.46$ (m, 2H, *o*-C_6H_5), 7.22 (m, 2H, *m*-C_6H_5), 6.97 (m, 1H, *p*-C_6H_5), 2.30 (m, 6H, PC*H*CH$_3$), 2.25 [t, J(P,H) = 1.2 Hz, 3H, =C(CH$_3$)], 2.02 [t, J(P,H) = 2.4 Hz, 3H, =C(CH$_3$)], 1.22 [dvt, $N = 13.0$, J(H,H) = 7.1 Hz, 18H, PCHC*H*$_3$], 1.16 [dvt, $N = 13.3$, J(H,H) = 7.1 Hz, 18H, PCHC*H*$_3$]; ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 41.5$ [d, J(Rh,P) = 144.0 Hz]; $C_{29}H_{53}OP_2Rh$ (582.6): calcd C 59.79, H 9.17; found C 58.89, H 9.47.

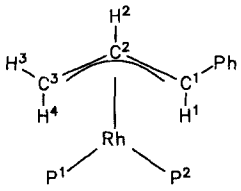
***trans*-[Rh{η^1-(*Z*)-C(Ph)=CHPh}(CNMe)(P*i*Pr$_3$)$_2$] (33)**: A solution of **8** (96 mg, 0.16 mmol) in toluene (5 mL) was treated at −30 °C with CNMe (8.9 μL, 0.16 mmol). After the solution had been stirred for 1 min, the solvent was removed, the residue was dissolved in toluene/pentane (5 mL; 1:2), and the solution stored for 7 d at −30 °C. Yellow crystals precipitated which were separated from the mother liquor, washed three times with 1 mL portions of pentane (−20 °C) and dried; yield 89 mg (76%); m.p. 129–131 °C (decomp.); IR (KBr): $\tilde{\nu} = 2080$ (C≡N) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 8.92$ [brs, 2H, Rh-C(=CHPh)-*o*-C_6H_5], 8.00 (m, 2H, *o*-C_6H_5), 7.74 [dt, J(Rh,H) = 2.1, J(P,H) = 2.0 Hz, 1H, =C*H*Ph], 7.23 [m, 6H, =CH-*m*-,*p*-C_6H_5 and C(=CHPh)-*m*-,*p*-C_6H_5], 2.22 (m, 6H, PC*H*CH$_3$), 2.22 [d, J(Rh,H) = 0.6 Hz, 3H, CNCH$_3$], 1.19 [dvt, $N = 13.2$, J(H,H) = 7.2 Hz, 18H, PCHC*H*$_3$], 1.16 [dvt, $N = 14.0$, J(H,H) = 6.9 Hz, 18H, PCHC*H*$_3$]; ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 39.43$ [d, J(Rh,P) = 147.9 Hz]; $C_{34}H_{56}NP_2Rh$ (643.7): calcd C 63.44, H 8.77, N 2.18; found C 63.06, H 9.09, N 1.88.

***trans*-[Rh{η^1-(*Z*)-C(Ph)=CHPh}(CN*t*Bu)(P*i*Pr$_3$)$_2$] (34)**: This was prepared as described for **33**, from **8** (105 mg, 0.17 mmol) and CN*t*Bu (20 μL, 0.17 mmol) as starting materials. Upon recrystallization from acetone yellow crystals were obtained; yield 85 mg (71%); m.p. 84 °C (decomp.); IR (KBr): $\tilde{\nu} = 2070$, 2030 (C≡N) cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 9.06$ (brs, 2H, =CH-*o*-C_6H_5), 8.08 (m, 2H, *o*-C_6H_5), 7.77 [dt, J(Rh,H) = 1.9, J(P,H) = 2.0 Hz, 1H, =C*H*R], 7.33 (m, 4H, *m*-C_6H_5), 7.07 (m, 2H, *p*-C_6H_5), 2.27 (m, 6H, PC*H*CH$_3$), 1.23 [dvt, $N = 13.5$, J(H,H) = 7.0 Hz, 18H, PCHC*H*$_3$], 1.16 [dvt, $N = 13.4$, J(H,H) = 6.8 Hz, 18H, PCHC*H*$_3$], 1.02 [s, 9H, C(CH$_3$)$_3$]; ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 38.9$ [d, J(Rh,P) = 148.8 Hz]; $C_{37}H_{62}NP_2Rh$ (685.8): calcd C 64.81, H 9.11, N 2.04; found C 65.03, H 9.36, N 2.03.

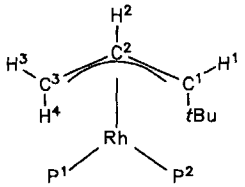
***trans*-[Rh{η^1-(*Z*)-C(Me)=CHPh}(CN*t*Bu)(P*i*Pr$_3$)$_2$] (35)**: This was prepared as described for **33**, from **18** (102 mg, 0.19 mmol) and CN*t*Bu (22 μL, 0.19 mmol) as starting materials. Yellow crystals; yield 98 mg (83%); m.p. 122 °C (decomp.); IR (KBr): $\tilde{\nu}$ = 2080, 2050 (C≡N) cm^{-1}; ^{1}H NMR (C_6D_6, 90 MHz, 35 °C): δ = 8.92 (brs, 2H, *o*-C_6H_5), 7.22 (m, 3H, *m*-, *p*-C_6H_5), 2.62 [s, 3H, Rh-C(CH$_3$)], 2.22 (m, 6H, PC*H*CH$_3$), 1.39 (dvt, *N* = 13.4, *J*(H,H) = 7.0 Hz, 18H, PCHC*H*$_3$), 1.14 [dvt, *N* = 12.2, *J*(H,H) = 6.4 Hz, 18H, PCHC*H*$_3$], 1.03 [s, 9H, C(CH$_3$)$_3$], signal of =C*H*R covered by signal of C_6H_5 protons; ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 188.7 [dt, *J*(Rh,C) = 28.0, *J*(P,C) = 14.0 Hz, Rh-*C*(R')=CHR], 158.1 [dt, *J*(Rh,C) = 47.7, *J*(P,C) = 16.5 Hz, Rh-*C*N*t*Bu], 146.8 (s, *ipso*-C_6H_5), 134.2 [t, *J*(P,C) = 3.8 Hz, Rh-C(R')=*C*HR], 129.9, 127.2, 122.8 (all s, C_6H_5), 54.5 [brs, *C*(CH$_3$)$_3$], 35.4 [s, Rh-C(*C*H$_3$)], 29.9 [s, C(*C*H$_3$)$_3$], 26.4 (vt, *N* = 17.8 Hz, PC*H*CH$_3$), 21.2, 19.9 (both s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 42.4 [d, *J*(Rh,P) = 153.8 Hz]; $C_{32}H_{60}NP_2Rh$ (623.7): calcd C 61.63, H 9.70, N 2.25; found C 62.01, H 9.82, N 2.09.

Reaction of compounds 27, 30, and 31 with acetic acid: A solution of **27** (60 mg, 0.10 mmol) or **30** (75 mg, 0.13 mmol) or **31** (65 mg, 0.11 mmol) in C_6D_6 (1 mL) was treated with an equimolar amount of acetic acid at room temperature. After the solution had been stirred for 4 h (**27**) or 11 h (**30**) or 5 h (**31**) a quantitative conversion of the starting material to [Rh(η^1-O_2CMe)(CO)(P*i*Pr$_3$)$_2$] (**38**)[11] and the corresponding olefin (*E*)-PhCH=CHPh (**36**) or (*E*)-PhCH=CHMe (**37**) or (*E*)-PhCH=CH–CH=CH$_2$ (**39**) was observed. The olefinic products were identified by ^{1}H and ^{13}C NMR spectroscopy [12].

[Rh(η^3-*syn*-CH$_2$CHCHPh)(P*i*Pr$_3$)$_2$] (40): A solution of **18** (50 mg, 0.08 mmol) in benzene (3 mL) was stirred for 12 h at room temperature. A smooth change of color from violet to yellow was observed. The solvent was removed in vacuo, the residue was dissolved in acetone (3 mL), and the solution was stored for 10 h at −78 °C. Orange crystals precipitated, which were separated from the mother liquor, washed twice with 2 mL portions of acetone (−20 °C) and dried; yield 37 mg (73%). A modified procedure is as follows: A solution of **5** (200 mg, 0.36 mmol) in ether (5 mL) was treated at −30 °C with a solution of MeMgI in ether (0.4 mL, 1.0 M). After the reaction mixture had been warmed to room temperature, it was stirred for 15 h, and then the solvent was removed. The residue was extracted with pentane (15 mL) and the extract brought to dryness in vacuo. The residue was dissolved in acetone (3 mL) and the solution worked up as described above; yield 168 mg (87%); m.p. 85 °C (decomp.); ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.33 (m, 2H, *o*-C_6H_5), 7.15 (m, 2H, *m*-C_6H_5), 6.98 (m, 1H, *p*-C_6H_5), 5.28 [ddd, *J*(H-2,H-4) = 12.2, *J*(H-1,H-2) = 10.7, *J*(H-2,H-3) = 6.7 Hz, 1H, H-2], 3.40 [dd, *J*(P-1,H-1) = 7.7, *J*(H-1,H-2) = 10.7 Hz, 1H, H-1], 3.12 [ddd, *J*(P-2,H-3) = 3.8, *J*(P-1,H-3) = 2.2, *J*(H-2,H-3) = 6.7 Hz, 1H, H-3], 2.18, 1.98 (both m, 6H, PC*H*CH$_3$), 2.09 [dd, *J*(P-2,H-4) = 5.6, *J*(H-2,H-4) = 12.2 Hz, 1H, H-4], 1.25 [dd, *J*(P,H) = 12.6, *J*(H,H) = 7.2 Hz, 9H, PCHC*H*$_3$], 1.16 [dd, *J*(P,H) = 12.5, *J*(H,H) = 7.2 Hz, 9H, PCHC*H*$_3$], 1.15 [dd, *J*(P,H) = 13.2, *J*(H,H) = 7.2 Hz, 9H, PCHC*H*$_3$], 1.11 [dd, *J*(P,H) = 13.3, *J*(H,H) = 7.2 Hz, 9H, PCHC*H*$_3$]; ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 146.7 [d, *J*(P,C) = 3.0 Hz, *ipso*-C_6H_5], 128.2, 126.7, 123.1 (all s, C_6H_5), 99.9 (m, C-2), 65.0 [ddd, *J*(Rh,C) = 27.6, *J*(P-1,C) = 6.9, *J*(P-2,C) = 2.7 Hz, C-1], 46.2 [ddd, *J*(Rh,C) = 21.0, *J*(P-2,C) = 9.4, *J*(P-1,C) = 5.2 Hz, C-3], 28.8 [d, *J*(P,C) = 13.9 Hz, P*C*HCH$_3$], 27.5 [d, *J*(P,C) = 13.1 Hz, P*C*HCH$_3$], 21.6 [d, *J*(P,C) = 3.5 Hz, PCH*C*H$_3$], 21.4 [d, *J*(P,C) = 2.5 Hz, PCH*C*H$_3$], 20.6, 20.1 (both s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 56.5 [dd, *J*(Rh,P) = 198.0, *J*(P,P) = 22.0 Hz, P-1], 46.2 [dd, *J*(Rh,P) = 189.5, *J*(P,P) = 22.0 Hz, P-2]; $C_{27}H_{51}P_2Rh$ (540.6): calcd C 59.99, H 9.51; found C 59.71, H 9.07.

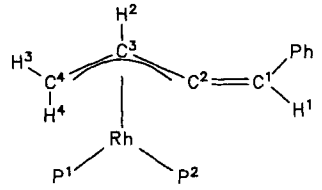


[Rh(η^3-*anti*-CH$_2$CHCH*t*Bu)(P*i*Pr$_3$)$_2$] (41): This was prepared as described for **40**, from **19** (70 mg, 0.13 mmol) in benzene (3 mL). Orange crystals; yield 57 mg (82%). The modified procedure using **6** (185 mg, 0.34 mmol) and a solution of MeMgI in ether (1.0 M) as starting materials could also be applied; yield 126 mg (71%); m.p. 84 °C (decomp.); ^{1}H NMR (C_6D_6, 400 MHz): δ = 4.86 [dddd, *J*(Rh,H-2) = 2.1, *J*(H-2,H-4) = 12.6, *J*(H-1,H-2) = 8.2, *J*(H-2,H-3) = 8.0 Hz, 1H, H-2], 3.86 [ddd, *J*(P-1,H-1) = 3.6, *J*(P-2,H-1) = 3.6, *J*(H-1,H-2) = 8.2 Hz, 1H, H-1], 2.74 [m, in ^{1}H{^{31}P}, brd, *J*(H-2,H-3) = 8.0 Hz, 1H, H-3], 2.28, 2.25 (both m, 6H, PC*H*CH$_3$), 2.05 (brdd, *J*(P-2,H-4) = 8.2, *J*(H-2,H-4) = 12.6 Hz, 1H, H-4), 1.29 [s, 9H, C(CH$_3$)$_3$], 1.29, 1.27 [both dd, *J*(P,H) = 13.4, *J*(H,H) = 7.2 Hz, 9H each, PCHC*H*$_3$], 1.17, 1.14 [both dd, *J*(P,H) = 13.6, *J*(H,H) = 7.3 Hz, 9H each, PCHC*H*$_3$]; ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 95.1 [ddd, *J*(Rh,C) = 5.7, *J*(P-1,C) = 1.2, *J*(P-2,C) = 1.2 Hz, C-2], 76.6 [ddd, *J*(Rh,C) = 25.9, *J*(P-1,C) = 10.6, *J*(P-2,C) = 4.4 Hz, C-1], 45.0 [ddd, *J*(Rh,C) = 29.9, *J*(P-2,C) = 8.3, *J*(P-1,C) = 5.2 Hz, C-3], 35.2 [dd, *J*(P-1,C) = 3.3, *J*(Rh,C) = 0.9 Hz, *C*(CH$_3$)$_3$], 34.4 [d, *J*(P-1,C) = 1.9, C(*C*H$_3$)$_3$], 29.6 [brd, *J*(P,C) = 12.0 Hz, PCHCH$_3$], 29.2 [brd, *J*(P,C) = 12.6 Hz, PCHCH$_3$], 21.8 [d, *J*(P,C) = 3.2 Hz, PCHCH$_3$], 21.4 [d, *J*(P,C) = 3.2 Hz, PCHCH$_3$], 20.2, 19.9 (both s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 49.0 [dd, *J*(Rh,P) = 206.7, *J*(P,P) = 19.1 Hz, P-1], 47.9 [dd, *J*(Rh,P) = 211.8, *J*(P,P) = 19.1 Hz, P-2]; $C_{25}H_{55}P_2Rh$ (520.6): calcd C 57.68, H 10.65; found C 57.36, H 10.97.



[Rh(η^3-C$_3$H$_5$)(P*i*Pr$_3$)$_2$] (42): This was prepared as described for **40**, from **20** (75 mg, 0.16 mmol) in benzene (3 mL). Yellow solid; yield 55 mg (73%). The modified procedure using **7** (175 mg, 0.36 mmol) and a solution of MeMgI (1.0 M) in ether could also be applied; yield 121 mg (72%). The compound was characterized by ^{1}H NMR spectroscopy [18b].

[Rh(η^3-*trans*-CH$_2$CHC=CHPh)(P*i*Pr$_3$)$_2$] (43): A solution of **11** (65 mg, 0.12 mmol) in benzene (3 mL) was stirred for 1 h at 45 °C. A smooth change of color from violet to orange-yellow occurred. After the solution had been cooled to room temperature, the solvent was removed, and the residue worked up as described for **40**. Orange crystals; yield 35 mg (55%). The modified procedure described for the preparation of **40**–**42** could also be applied, using **5** (210 mg, 0.37 mmol) and a solution of CH$_2$=CHMgBr in THF (1.0 M) as starting materials; yield 126 mg (61%); m.p. 80 °C (decomp.): ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.81 (m, 2H, *o*-C_6H_5), 7.28 (m, 2H, *m*-C_6H_5), 7.09 (m, 1H, *p*-C_6H_5), 6.34 (m, 1H, H-1), 4.71 (m, 1H, H-2), 3.13 [ddd, *J*(P-1,H) = 2.5, *J*(P-2,H) = 2.5, *J*(H-2,H-3) = 7.4 Hz, 1H, H-3], 2.41, 2.14 (both m, 6H, PC*H*CH$_3$), 1.29 [dd, *J*(P,H) = 12.9, *J*(H,H) = 7.2 Hz, 9H, PCHC*H*$_3$], 1.22 [dd, *J*(P,H) = 12.0, *J*(H,H) = 7.3 Hz, 9H, PCHC*H*$_3$], 1.16 [dd, *J*(P,H) = 12.5, *J*(H,H) = 7.2 Hz, 9H, PCHC*H*$_3$], 1.10 [dd, *J*(P,H) = 12.6, *J*(H,H) = 7.1 Hz, 9H, PCHC*H*$_3$], signal of H-4 covered by PCH signal at δ = 2.14; ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 171.2 (m, C-2), 140.1 [d, *J*(P,C) = 5.0 Hz, *ipso*-C_6H_5], 128.8, 126.4, 124.7 (all s, C_6H_5), 111.8 (s, C-1), 78.7 [d, *J*(Rh,C) = 3.9 Hz, C-3], 47.9 [ddd, *J*(Rh,C) = 25.1, *J*(P-2,C) = 5.9, *J*(P-1,C) = 4.9 Hz, C-4], 28.4 [d, *J*(P,C) = 12.2 Hz, PCHCH$_3$], 27.6 [d, *J*(P,C) = 15.1 Hz, PCHCH$_3$], 21.4 [d, *J*(P,C) = 2.0 Hz, PCH*C*H$_3$], 20.8 [d, *J*(P,C) = 2.6 Hz, PCH*C*H$_3$], 20.6, 20.3 (both s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 52.8 [dd, *J*(Rh,P) = 197.0, *J*(P,P) = 21.9 Hz, P-1], 46.8 [dd, *J*(Rh,P) = 160.5, *J*(P,P) = 21.9 Hz, P-2]; $C_{28}H_{51}P_2Rh$ (552.6): calcd C 60.86, H 9.30; found C 60.49, H 9.00.



[Rh(η^3-*trans*-CH$_2$CHC=CH*t*Bu)(P*i*Pr$_3$)$_2$] (44): This was prepared as described for **43**, either from **12** (55 mg, 0.10 mmol) or from **6** (240 mg, 0.45 mmol) and a solution of CH$_2$=CHMgBr in THF (0.6 mL, 1.0 M) as starting materials. Orange microcrystalline solid; yield 34 mg (62%) from **12** and 166 mg (69%) from **6**; m.p. 79 °C (decomp.); ^{1}H NMR (C_6D_6, 400 MHz): δ = 5.14 (m, 1H, H-1), 4.50 (m, 1H, H-2), 2.98 [ddd, *J*(P-1,H) = 2.6, *J*(P-2,H) = 2.6, *J*(H-2,H-3) = 8.0 Hz, 1H, H-3], 2.37, 2.17 (both m, 6H, PC*H*CH$_3$), 1.93 [dd, *J*(P-2,H) = 6.7, *J*(H-2,H-4) = 11.7 Hz, 1H, H-4], 1.30 [s, 9H, C(CH$_3$)$_3$], 1.29 [dd, *J*(P,H) = 11.9, *J*(H,H) = 7.4 Hz, 9H, PCHC*H*$_3$], 1.23 [dd, *J*(P,H) = 11.7, *J*(H,H) = 7.2 Hz, 9H, PCHC*H*$_3$], 1.18 [dd, *J*(P,H) = 12.9, *J*(H,H) = 7.5 Hz, 9H, PCHC*H*$_3$], 1.13 [dd, *J*(P,H) = 11.9, *J*(H,H) = 7.3 Hz, 9H, PCHC*H*$_3$], for assignment of H-1–H-4 see **43**: ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 161.0 [ddd, *J*(Rh,C) = 43.8, *J*(P-1,C) = 18.3, *J*(P-2,C) = 9.2 Hz, C-2], 120.3 (s, C-1), 77.0 [d, *J*(Rh,C) = 4.0 Hz, C-3], 47.6 [ddd, *J*(Rh,C) = 26.4, *J*(P-2,C) = 6.9, *J*(P-1,C) = 5.7 Hz, C-4], 34.2 [d, *J*(P-1,C) = 5.6 Hz, *C*(CH$_3$)$_3$], 31.2 [s, C(*C*H$_3$)$_3$], 28.2 [d, *J*(P,C) = 11.9 Hz, PCHCH$_3$], 27.3 [d, *J*(P,C) = 14.2 Hz, PCHCH$_3$], 21.5 [d, *J*(P,C) = 3.8 Hz, PCH*C*H$_3$], 21.0 [d, *J*(P,C) = 3.6 Hz, PCH*C*H$_3$], 20.6, 20.2 (both s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 52.2 [dd, *J*(Rh,P) = 196.8,

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J(P,P) = 20.9 Hz, P-1], 48.0 [dd, J(Rh,P) = 164.6, J(P,P) = 20.9 Hz, P-2]; $C_{26}H_{55}P_2Rh$ (532.6): calcd C 58.64, H 10.41; found C 58.21, H 10.01.

Preparation of *trans*-[Rh(C≡CR)(C_2H_4)($PiPr_3$)$_2$] (45, 46) from 11, 12: A solid sample of **11** (60 mg, 0.11 mmol) or **12** (75 mg, 0.14 mmol) was stored under argon in the absence of light for 14 d at room temperature. A slow change of color from violet to orange-brown occurred. The solid was dissolved in acetone (2 mL) and after the solution had been stored for 10 h at −78 °C orange crystals precipitated. They were separated from the mother liquor, washed twice with 1 mL portions of acetone (−20 °C) and dried; yield 49 mg (81%) of **45** and 52 mg (69%) of **46**. Both compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy [8].

Reaction of compounds 40, 41, and 44 with acetic acid: A solution of **40** (43 mg, 0.08 mmol) or **41** (42 mg, 0.08 mmol) or **44** (43 mg, 0.08 mmol) in C_6D_6 (0.5 mL) was treated at 10 °C with an equimolar amount of acetic acid. A smooth change of color from orange to red occurred. After the solution had been stored for 30 min at room temperature, a quantitative conversion of the starting material to [Rh(η^2-O_2CMe)($PiPr_3$)$_2$] (**47**) and the corresponding olefin had taken place. The olefinic products (*E*)-PhCH=CHMe (**37**), (*Z*)-CH_2=CHCH=CH*t*Bu (**48**) and (*E*)/(*Z*)-MeCH=CH*t*Bu (**49a/49b**, ratio 70:30) were identified by ^{1}H and ^{13}C NMR spectroscopy [12,25]. For the isolation of **47**, the olefin and the solvent were removed in vacuo, the residue dissolved in acetone (1 mL), and the solution stored at −78 °C for 12 h. Red crystals precipitated, which were washed twice with 1 mL portions of acetone (−20 °C) and dried; yield 34 mg (89%). Compound **47** was identified by ^{1}H and ^{31}P NMR spectroscopy [18b].

Preparation of 5 from 47: A solution of **47** (110 mg, 0.23 mmol) in benzene (3 mL) was treated at 10 °C with phenylacetylene (24 μL, 0.23 mmol) and then stirred for 3 h at room temperature. The solution was chromatographed on Al_2O_3 (neutral, activity grade III, height of column 8 cm, diameter 1.5 cm) with hexane. During the chromatographic procedure, a characteristic change of color from orange to blue took place on the column. The blue fraction was brought to dryness in vacuo, and the residue was identified as **5** by ^{1}H and ^{13}C NMR spectroscopy [4a]; yield 123 mg (95%).

X-ray structural analysis of 30: Single crystals were grown from acetone at −78 °C. Crystal data (from 23 reflections, $10° < \theta < 14°$): monoclinic, space group $P2_1/n$ (no. 14); a = 10.640(3) Å, b = 29.070(3) Å, c = 15.476(5) Å, b = 108.05(1)°, V = 3142.3(9) Å^3, Z = 4, ρ_{calcd} = 1.23 g cm^{-3}, $\delta(Mo_{K\alpha})$ = 6.5 cm^{-1}, T = 293 K; crystal size 0.13 × 0.23 × 0.30 mm; Enraf–Nonius CAD4 diffractometer, $Mo_{K\alpha}$ radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 16.4); $w/2\theta$ scan, max. 2θ = 48°; 4157 reflections measured, 3563 independent reflections, 2569 regarded as being observed [$F_0 > 3\sigma(F_0)$]; intensity data were corrected for Lorentz and polarization effects, empirical absorption correction (ψ-scan method) was applied, minimum transmission was 94.9%. The structure was solved by direct methods (SHELXS-86); atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares (298 parameters, unit weights, Enraf–Nonius SDP) [31]. The positions of all hydrogen atoms were calculated according to ideal geometry (C–H distance 0.95 Å) and were included in the structure factor calculation in the last refinement cycle. R = 0.034, R_w = 0.035; reflex/parameter ratio 8.62; residual electron density +0.37/−0.24 e Å^{-3} [32].

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[32] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1220-42. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).