A New Family of Organometallic Rhodium Complexes with [Rh(P*i*Pr$_2$Ph)$_2$] and [Rh(P*i*PrPh$_2$)$_2$] as Molecular Units

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Dedicated to Professor Walter Siebert on the occasion of his 65th birthday

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The π-allyl complexes [Rh(η^3-C_3H_5)(PR$_3$)$_2$] [PR$_3$ = P*i*Pr$_2$Ph (**4**), P*i*PrPh$_2$ (**5**)], prepared from [RhCl(C_8H_{14})$_2$]$_2$, PR$_3$ and the Grignard reagent C_3H_5MgBr, react with carboxylic acids and *p*-toluenesulfonic acid to give the chelate compounds [Rh(κ^2-O_2CR′)(PR$_3$)$_2$] (**8**–**10**) and [Rh{κ^2-O_2S(O)-*p*-Tol}(PR$_3$)$_2$] (**11**, **12**), respectively. While the reactions of **8**, **10** and **12** with CO afford the square-planar rhodium(I) complexes **13**–**15** with monodentate carboxylato and tosylato ligands, treatment of **8**–**10** and **11**, **12** with H_2 leads to the formation of the octahedral dihydridorhodium(III) derivatives [RhH$_2$(κ^2-O_2CR′)(PR$_3$)$_2$] (**16**–**18**) and [RhH$_2${κ^2-O_2S(O)-*p*-Tol}(PR$_3$)$_2$] (**19**, **20**). Similarly to CO, internal alkynes RC≡CCO_2Me (R = CO_2Me, Me) react with **8** and **9** by partial opening of the chelate bond to yield the π-alkyne complexes **21**–**23**, of which **23** with R = Me is quite labile and smoothly regenerates the starting material. In contrast, the reactions of **8** and **9** with terminal alkynes HC≡CR (R = Ph, CO_2Me) afford six-coordinate alkynyl(vinyl)rhodium(III) compounds **24**–**26** with a different stereochemistry at the C=C double bond depending on the substituent R. From **8** and HC≡CCH(Cl)Me the octahedral allenyl complex [RhCl(CH=C=CHMe)(κ^2-O_2CR′)(P*i*PrPh$_2$)$_2$] (**27**) is obtained, the molecular structure of which has been determined by X-ray crystallography. The reaction of [Rh(κ^1-O_2CR){η^2-C_2(CO_2Me)$_2$}(P*i*PrPh$_2$)$_2$] (**21**, **22**) with HC≡CPh also leads to the six-coordinate alkynyl(vinyl)rhodium(III) compounds **28**, **29**, which upon treatment with Me_3SiCl and thermolysis are stepwise converted into the four-coordinate π-enyne complex *trans*-[RhCl{η^2-Ph*C*≡*C*C(CO_2Me)=CHCO_2Me}(P*i*PrPh$_2$)$_2$] (**31**). The reaction of **31** with CO generates the uncoordinated substituted enyne. The rhodium(I) vinylidene complexes *trans*-[Rh(C≡CR′)(=C=CHR)(P*i*PrPh$_2$)$_2$] (**36**–**38**) were prepared in two steps from the tosylato complex **12** and terminal alkynes; they react with CO via migratory insertion to give the square-planar enynyl compounds *trans*-[Rh{η^1-C(C≡CR)=CHR′}(CO)(P*i*PrPh$_2$)$_2$] (**39**–**41**).

Introduction

In the context of our investigations on low-valent organorhodium compounds,[1] we recently reported a high-yield synthesis of the π-allyl complexes [Rh(η^3-2-C_3H_4R)(P*i*Pr$_3$)$_2$] (R = H, Me, Ph) which readily react with Brønsted acids by cleavage of the allyl-metal bond.[2] If terminal alkynes HC≡CR were used as acidic substrates, the alkynyl(vinylidene)rhodium(I) compounds *trans*-[Rh(C≡CR)(=C=CHR)(P*i*Pr$_3$)$_2$] were obtained which, in the presence of CO or isocyanides, undergo an intramolecular C−C coupling process.[3] Since we observed that the course of the reactions of rhodium(I) compounds [Rh(X)(P*i*Pr$_3$)$_2$] (where X could be a carboxylate or tosylate) with HC≡CR depends on both the anionic ligand X$^-$ and the substituent R of the alkyne, we became interested to find out whether the nature of the phosphane would also have an influence on the composition of the products. In a recent paper, some evidence for this assumption was already presented.[4] The present article describes preparative routes to four-coordinate carboxylato- and tosylatorhodium(I) complexes with P*i*PrPh$_2$ and P*i*Pr$_2$Ph as ligands and reports in detail on their reactivity toward internal and terminal alkynes.

Results and Discussion

The method recently used by us for the synthesis of [Rh(η^3-C_3H_5)(P*i*Pr$_3$)$_2$][2] could also be applied for the preparation of the related complexes **4** and **5** (Scheme 1). Treatment of a suspension of **1** in toluene with P*i*Pr$_2$Ph or P*i*PrPh$_2$ in 1:4 molar ratio, followed by the addition of a solution of the Grignard reagent C_3H_5MgBr in ether, results in the formation of the π-allylrhodium(I) compounds **4** and **5**, which were isolated as yellow solids in about 80% yield. If the violet solution, formed upon the addition of P*i*Pr$_2$Ph or P*i*PrPh$_2$ to the starting material **1** in toluene, is dried in vacuo, the bis(phosphane)rhodium(I) derivatives **2** and **3** were obtained. These dimeric complexes are some-

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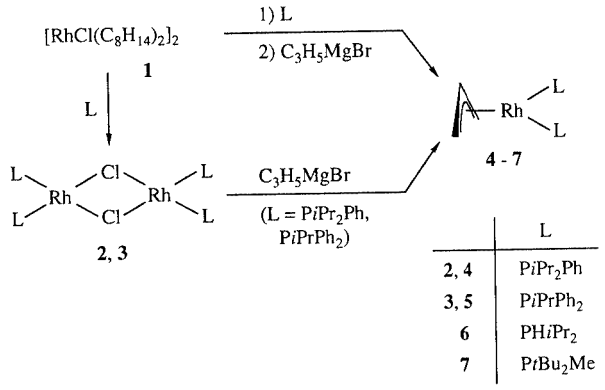
what less air-sensitive than the triisopropylphosphane counterpart $[RhCl(PiPr_3)_2]_2$ [5] and can be stored under argon at room temperature without decomposition. The ^{31}P NMR spectra of **2** and **3** show the expected doublet with a large ^{31}P-^{103}Rh coupling constant of ca. 198 Hz that is typical for rhodium(I) compounds with $[Rh(PR_3)_2]$ as a building block and *cis*-disposed phosphane ligands.[2,4,6]

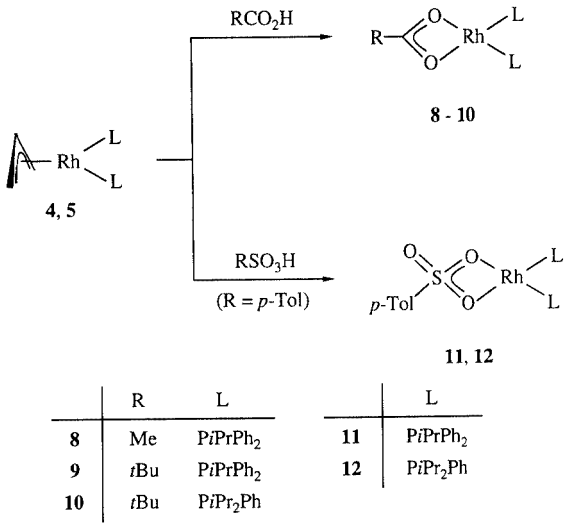


	L
2, 4	$PiPr_2Ph$
3, 5	$PiPrPh_2$
6	$PHiPr_2$
7	$PtBu_2Me$

Scheme 1

While the reactions of **2** and **3** with a twofold excess of the Grignard reagent C_3H_5MgBr also lead to the generation of **4** and **5**, the preparative route using **1** as the precursor is more convenient. It can also be applied for the synthesis of **6** and **7** with $PHiPr_2$ and $PtBu_2Me$ as the phosphane ligands. The ^1H NMR spectra of the π-allylrhodium(I) complexes **4** and **6** exhibit, besides the expected sets for the C_3H_5 protons, four resonances for the protons of the diastereotopic methyl groups of the $PiPr_2$ moieties, which are split into doublets of doublets due to ^{31}P-^1H and ^1H-^1H coupling. Moreover, the ^1H NMR spectrum of **6** shows a doublet of triplets at $\delta = 4.06$ with a large ^{31}P-^1H coupling constant of 256.5 Hz that is characteristic of a P-bonded hydrogen atom. The observation of two distinct signals for the nuclei of the *syn* and the *anti* protons of the terminal allylic CH_2 groups indicate that in solution at room temperature the $(\eta^3\text{-}C_3H_5)Rh$ unit is rigid and does not undergo an η^3-η^1-η^3 rearrangement.[7]

The π-allylic complexes **4** and **5** react smoothly with equimolar amounts of carboxylic acids or *p*-toluenesulfonic acid by cleavage of the allyl-metal bond (Scheme 2). The apparently more simple synthetic method, namely the reaction of **2** or **3** with RCO_2Na or RSO_3Na, led to mixtures of products which could not be separated by fractional crystallization or chromatographic techniques. Both the rhodium carboxylates **8**−**10** and the rhodium tosylates **11** and **12** are red air-sensitive solids which, with the exception of pentane, are readily soluble in common organic solvents. The IR spectra of the carboxylato compounds **8**−**10** display two bands in the region of 1425−1445 and 1480−1510 cm^{-1} assigned to the symmetric and asymmetric OCO stretching modes. According to various data from the literature,[8] there is no doubt that the RCO_2^- ligands of **8**−**10** are coordinated in a chelating and not in a bridging fashion as found for the bis(ethene)rhodium(I) and dicarbonylrhodium(I) derivatives $[\{Rh(\mu\text{-}O_2CR)(C_2H_4)_2\}_2]$ and $[\{Rh(\mu\text{-}O_2CR)(CO)_2\}_2]$, respectively.[9] We assume that a chelating bonding mode also results for the RSO_3^- unit in the complexes **11** and **12**, as has been confirmed for the bis(triisopropylphosphane) compound $[Rh\{\kappa^2\text{-}O_2S(O)R\}(PiPr_3)_2]$ (R = *p*-Tol; Tol = C_6H_4Me) by X-ray crystallography.[10]



	R	L
8	Me	$PiPrPh_2$
9	*t*Bu	$PiPrPh_2$
10	*t*Bu	$PiPr_2Ph$

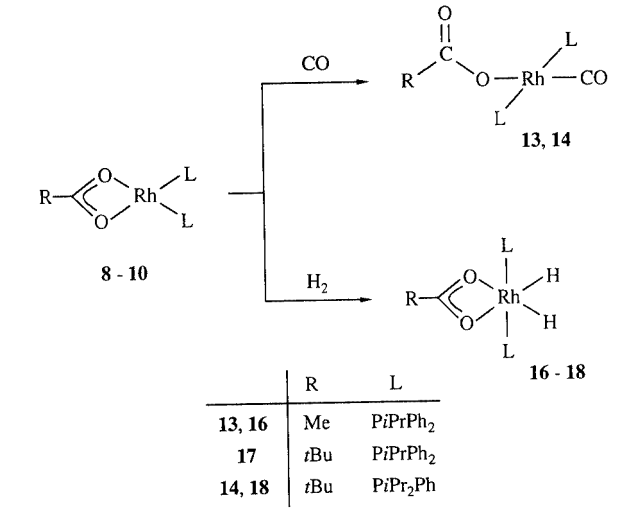
	L
11	$PiPrPh_2$
12	$PiPr_2Ph$

Scheme 2

With regard to the mechanism of formation of **8**−**10** and **11**, **12** from the π-allyl metal precursors **4** and **5**, we assume that the primary step consists of an oxidative addition of the acid HX to the rhodium(I) center to give the six-coordinate rhodium(III) intermediates $[RhH(\kappa^1\text{-}X)(\eta^3\text{-}C_3H_5)(PR_3)_2]$ (X = O_2CR, O_3SR), which upon reductive elimination of propene afford the products. We note that upon treatment of $[Rh(\eta^3\text{-}C_3H_5)(PiPr_3)_2]$ with an equimolar amount of CF_3CO_2H in pentane at −20 °C a stable compound $[RhH(\kappa^1\text{-}O_2CCF_3)(\eta^3\text{-}C_3H_5)(PiPr_3)_2]$ has been isolated which reacts at 40 °C to give $[Rh(\kappa^2\text{-}O_2CCF_3)(PiPr_3)_2]$ and C_3H_6.[2]

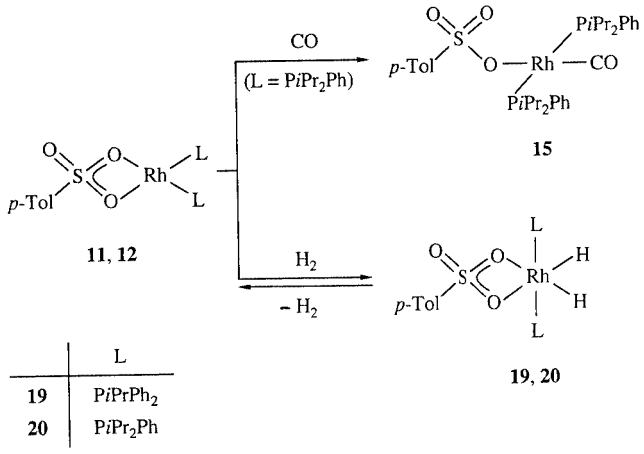
In the presence of CO, the carboxylato complexes as well as the tosylato derivatives are quite labile and react by partial opening of the chelate bond. This behavior has been exemplified by the preparation of the mononuclear compounds **13**−**15** (Scheme 3 and 4), which were isolated as pale-yellow, almost air-stable solids in 93−98% yield. In contrast to **8** and **10**, the IR spectra of **13** and **14** confirm that the RCO_2^- units are coordinated in a monodentate fashion. The two phosphane ligands of **13**−**15** are *trans*-disposed, which is illustrated by the appearance of one doublet in the ^{31}P NMR spectra, the respective ^{31}P-^{103}Rh coupling constant being significantly smaller than for the starting materials **8**, **10** and **12** with a *cis*-disposed $Rh(PR_3)_2$ moiety.

The carboxylato compounds **8**−**10** also react at room temperature with dihydrogen to give the octahedral dihydridorhodium(III) complexes **16**−**18** by oxidative addition. The white solids are much less sensitive towards air than the rhodium(I) precursors and can be stored under argon for weeks. The ^{31}P NMR spectra of **16**−**18** show only one



	R	L
13, 16	Me	P*i*PrPh$_2$
17	*t*Bu	P*i*PrPh$_2$
14, 18	*t*Bu	P*i*Pr$_2$Ph

Scheme 3



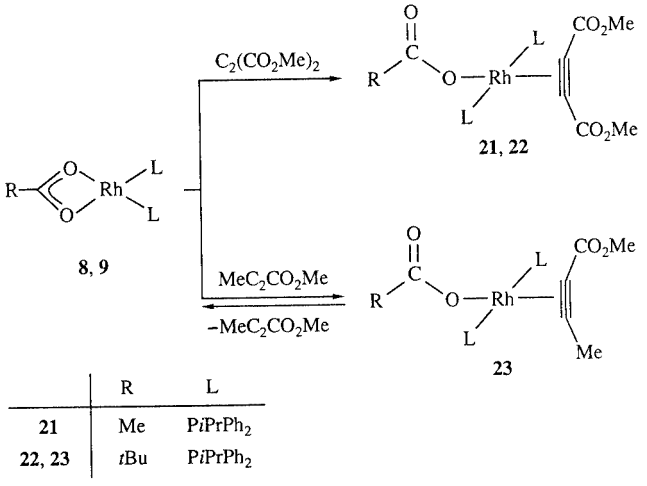
	L
19	P*i*PrPh$_2$
20	P*i*Pr$_2$Ph

Scheme 4

resonance, indicating that the two phosphanes remain in a *trans* disposition. In the ^{1}H NMR spectra, there is also only one set of signals at $\delta = -22.0$ to -22.7 for the hydride ligands, which is in agreement with the proposed structure shown in Scheme 3.

The tosylato derivatives **11** and **12** have the same reactivity towards H_2 as the carboxylato derivatives. However, the isolated dihydrido complexes **19** and **20** are less stable than **16**−**18** and in vacuo slowly lose dihydrogen to regenerate the starting materials **11** and **12**. Therefore, it is necessary that they are stored at low temperature under a H_2 atmosphere. Since the ^{1}H and ^{31}P NMR spectroscopic data of **19** and **20** are similar to those of **16**−**18**, we assume that at 25 °C the two possible stereoisomers rapidly interconvert on the NMR time scale. At −78 °C in [D$_8$]toluene, there is only a slight broadening of the single resonance in the ^{31}P NMR spectra, which indicates that even under these conditions the interconversion of the two isomers should be very fast.

The reactions of the carboxylato complexes **8** and **9** with $C_2(CO_2Me)_2$ proceed analogously to those with CO. Treatment of the starting materials in benzene with an equimolar amount of the alkyne at room temperature leads to an almost instantaneous change of color from dark red to yellow and finally affords the products **21** and **22** (see Scheme 5) in about 85% yield. The ^{1}H and ^{31}P NMR spectra of **21** and **22** are, with respect to the P*i*PrPh$_2$ ligands, quite similar to those of the carbonyl compound **13**, and thus there is no doubt that the coordination geometry around the metal center is square planar. The IR spectra of **21** and **22** show the ν(C≡C) stretching mode at 1810 cm^{-1} (for **21**) and 1785 cm^{-1} (for **22**), the decrease of about 450 cm^{-1} relative to free $C_2(CO_2Me)_2$ being in agreement with the strong π-acceptor character of the electron-poor alkyne.

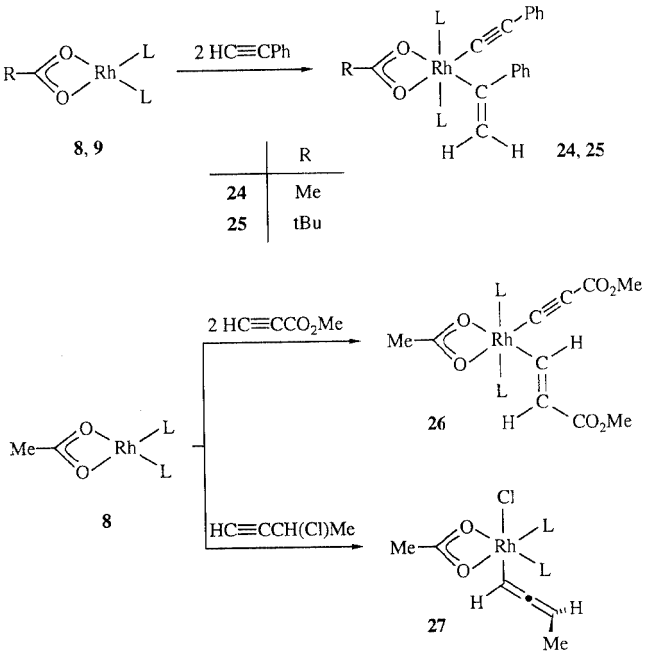


	R	L
21	Me	P*i*PrPh$_2$
22, 23	*t*Bu	P*i*PrPh$_2$

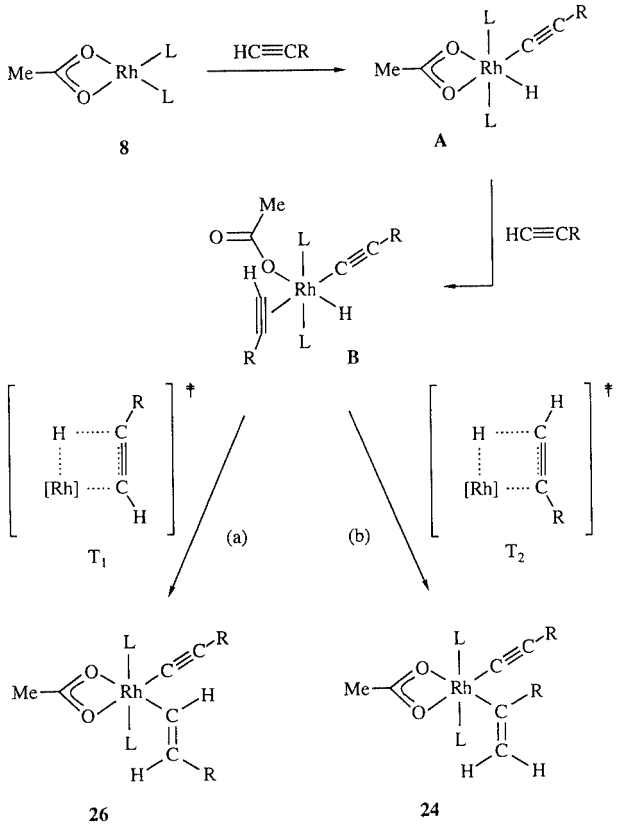
Scheme 5

While compound **8** does not react with MeC≡CCO$_2$Me in toluene at −20 °C, the corresponding reaction for **9** with MeC≡CCO$_2$Me under the same conditions takes place but is reversible. Only if the reaction mixture formed after stirring a solution of **9** and the alkyne in toluene at −20 °C for 2 h is worked-up rather quickly, and the crude product recrystallized from hexane at −78 °C, can a light yellow solid with the analytical composition corresponding to **23** be isolated. The ^{1}H and ^{31}P NMR spectra (measured in [D$_8$]toluene at −30 °C) differ only slightly from those of **22** and thus deserve no further comment.

The reactions of **8** and **9** with *terminal* alkynes take a different course to those of the same starting materials with $C_2(CO_2Me)_2$. Treatment of the carboxylato rhodium(I) complexes with two equiv. of phenylacetylene in toluene at −50 °C leads unexpectedly to the formation of the octahedral alkynyl(vinyl)rhodium(III) compounds **24** and **25** (Scheme 6), which were isolated as pale-yellow, only moderately air-sensitive solids in excellent yields. Although we attempted to detect the supposed intermediates [RhH(C≡CPh)(κ^2-O$_2$CR)(P*i*PrPh$_2$)$_2$] by monitoring the ^{1}H NMR spectra in [D$_8$]toluene at low temperature, we failed to observe the characteristic signals for such hydridometal species. Typical spectroscopic features of **24** and **25** are the two singlets for the stereochemically different protons of the C(Ph)=CH$_2$ ligand at about $\delta = 5.4$ to 6.0 in the ^{1}H NMR



Scheme 6. (L = P*i*PrPh$_2$)



Scheme 7. (L = P*i*PrPh$_2$)

spectrum and the doublet of triplets resonances for the alkynyl and vinyl carbon atoms in the region of δ = 100 to 150 in the ^{13}C NMR spectra. The ^{31}P NMR spectra of **24** and **25** display a sharp doublet at about δ = 30 with a ^{31}P-^{103}Rh coupling constant of 105−106 Hz that is in agreement with a *trans*-disposed Rh(PR$_3$)$_2$ unit.

The reaction of the acetato compound **8** with methyl propiolate also affords an octahedral alkynyl(vinyl)rhodium(III) complex **26** but with a different stereochemistry at the C=C double bond than **24**. While the ^{1}H NMR spectrum of **24** displays the signals for the vinylic protons at δ = 5.87 and 5.42, the ^{1}H NMR spectrum of **26** exhibits the two resonances at δ = 9.18 and 6.33. Both are split into doublets of doublets of triplets due to ^{1}H-^{1}H, ^{1}H-^{31}P and ^{1}H-^{103}Rh coupling. There is no doubt, in particular owing to the size of the ^{1}H-^{1}H coupling constant of 14.6 Hz, that in **26** the two protons at the C=C double bond are *trans* to each other. The same configuration has been found for the bis(triisopropylphosphane) complex [Rh(κ^2-O$_2$CCH$_3$)(C≡CCO$_2$Me){(*E*)-CH=CHCO$_2$Me}(P*i*Pr$_3$)$_2$], which was prepared in a stepwise manner from [RhH$_2$(κ^2-O$_2$CCH$_3$)(P*i*Pr$_3$)$_2$] and three equiv. of HC≡CCO$_2$Me under similar conditions.[11,12]

A proposal for the mechanism of the reactions of **8** with alkynes HC≡CR is outlined in Scheme 7. Although we have no evidence for the formation of intermediate **A**, we assume, in analogy to the reaction of [Rh(κ^2-O$_2$CCH$_3$)(P*i*Pr$_3$)$_2$] with phenylacetylene,[11] that in the first step such an alkynyl(hydrido)rhodium(III) species is generated. The addition of a second molecule of HC≡CR should give intermediate **B**. With regard to the next step, it probably depends on steric as well as electronic effects whether pathway (a) or (b) with the four-center transition states T$_1$ and T$_2$, respectively, is preferred. The above-mentioned dihydridorhodium compound [RhH$_2$(κ^2-O$_2$CCH$_3$)(P*i*Pr$_3$)$_2$], containing two phosphane ligands that are more bulky than P*i*PrPh$_2$, reacts with both HC≡CPh and HC≡CCO$_2$Me to give insertion products with a Rh−CH=CHR stereochemistry.[11,12] Moreover, the reaction of the six-coordinate hydridoiridium(III) compound [IrHCl(C≡CCO$_2$Me){κ^1-*P*-*i*Pr$_2$P(CH$_2$)$_2$OMe}{κ^2-*P*,*O*-*i*Pr$_2$P(CH$_2$)$_2$OMe}] with HC≡CCO$_2$Me also leads to an alkynyl(vinyl) complex with an Ir−CH=CHR linkage.[13]

In contrast to HC≡CPh and HC≡CCO$_2$Me, the chloro-substituted alkyne HC≡CCH(Cl)Me reacts with one equiv. of **8** to give the allenylrhodium(III) compound **27** in 88% yield instead of an alkynyl complex (see Scheme 6). In this process a migration of the chloride from the γ-carbon atom of the alkyne to rhodium takes place, followed by the formation of a σ bond between the metal and the remaining C$_3$ unit. Although a variety of allenyl-transition metal complexes have been prepared with allenyl halides as substrates, there is ample evidence that propargylic chlorides or propargylic alcohols can also be used to generate an M−CH=C=CRR′ bond.[14,15] Characteristic spectroscopic data for the allenyl ligand in **27** are the signals for the =CH and =CCH$_3$ protons at δ = 4.96 and 1.53, respectively, which not only couple to each other but also exhibit a ^{1}H-^{1}H coupling with the proton at the α-carbon atom. The ^{13}C NMR spectrum of **27** displays the resonances for the allenyl carbons at δ = 198.1, 87.4 and 83.0, of which only that of the metal-bound C atom at δ = 87.4 shows a ^{13}C-^{31}P and ^{13}C-^{103}Rh coupling.

The result of the X-ray crystal structure analysis of **27** is shown in Figure 1. The coordination geometry around rhodium is distorted octahedral with the two phosphanes *cis* and the chloride and the allenyl ligand *trans* to each other. Both the O1−Rh−O2 and P1−Rh−P2 bond angles deviate significantly from 90°, which is due on one hand to the bite angle of the chelating acetate and on the other to steric hindrance between the substituents at the two phosphorus atoms. The Cl−Rh−C1 axis is somewhat bent, the bond angle of 171.0(2)° being nearly identical to that of the octahedral allenylosmium complex [OsCl$_2$(η^1-CH=C=CPh$_2$)(NO)(P*i*Pr$_3$)$_2$] [170.5(1)°].[15] The Rh−C1 distance [2.052(5) Å] is slightly shorter than in *trans*-[Rh{η^1-(*Z*)-C(CH=CH$_2$)=CHPh}(CO)(P*i*Pr$_3$)$_2$] [2.088(5) Å][16] and *trans*-[Rh{η^1-C(CN)=CAn$_2$}(CO)(P*i*Pr$_3$)$_2$] [2.106(4) Å; An = *p*-C$_6$H$_4$OMe][17] but significantly longer than in the vinylrhodium cation [Rh{η^1-(*E*)-CH=CHCy}(κ^2-acac)(P*i*Pr$_3$)$_2$]$^+$ [1.98(1) Å].[18] The Rh−C1−C2 bond angle is almost exactly 120° and thus in agreement with the sp^2-hybridisation at the α-carbon atom of the C$_3$ chain. In close analogy to uncoordinated allenes,[19] the two planes [Rh,C1,C2,H1] and [C2,C3,C4,H3] are nearly perpendicular to each other, with a dihedral angle of 88(2)°.

Whereas attempts to reductively eliminate the enyne CH$_2$=C(Ph)−C≡CPh by warming or irradiating solutions of **24** or **25** failed, treatment of **25** with excess phenylacetylene in benzene at room temperature leads to the dimerization of the alkyne. The catalytic C−C coupling process can also be initiated by the carboxylatorhodium(I) compound **9** (the starting material for the preparation of **25**) and gives, under the conditions described in the Exp. Sect., the branched enyne CH$_2$=C(Ph)−C≡CPh almost exclusively. According to the ^{1}H NMR spectrum of the solution, taken after 80% of phenylacetylene has been consumed, the isomers (*E*)- and (*Z*)-PhCH=CH−C≡CPh are formed in less than 1% yield. In this context we note that Vinogradov et al. previously reported that [RhCl(PMe$_3$)$_3$] catalyses the dimerization of terminal alkynes HC≡CR (R = C$_3$H$_7$, C$_4$H$_9$, C$_6$H$_{13}$) to afford a mixture of the enynes CH$_2$=C(R)−C≡CR and (*E*)-RCH=CH−C≡CR with a selectivity of 95−98%.[20] In this case the formation of alkynyl(vinyl)rhodium(III) compounds as intermediates has been postulated.

An enyne of the composition RCH=C(R)−C≡CPh with R = CO$_2$Me has been generated from the alkyne complexes **21** and **22** in a stepwise manner. Treatment of a solution of **21** or **22** in dichloromethane at −20 °C with phenylacetylene leads instantaneously to a change of color from pale-yellow to red, followed quickly by a reverse change of color from red to pale-yellow. After removal of the solvent and extraction of the residue with acetone, the pale-yellow air-sensitive solids **28** and **29**, with an analytical composition corresponding to 1:1 adducts of the starting materials and HC≡CPh, could be isolated (Scheme 8). Both the IR and NMR spectra of **28** and **29** indicate that the two alkynes have been converted to an alkynyl and a vinyl ligand in the coordination sphere of the metal, the latter being generated from the coordinated disubstituted alkyne and the acidic hydrogen atom of phenylacetylene. The supposed *cis*-position of H and Rh at the C=C double bond is supported by

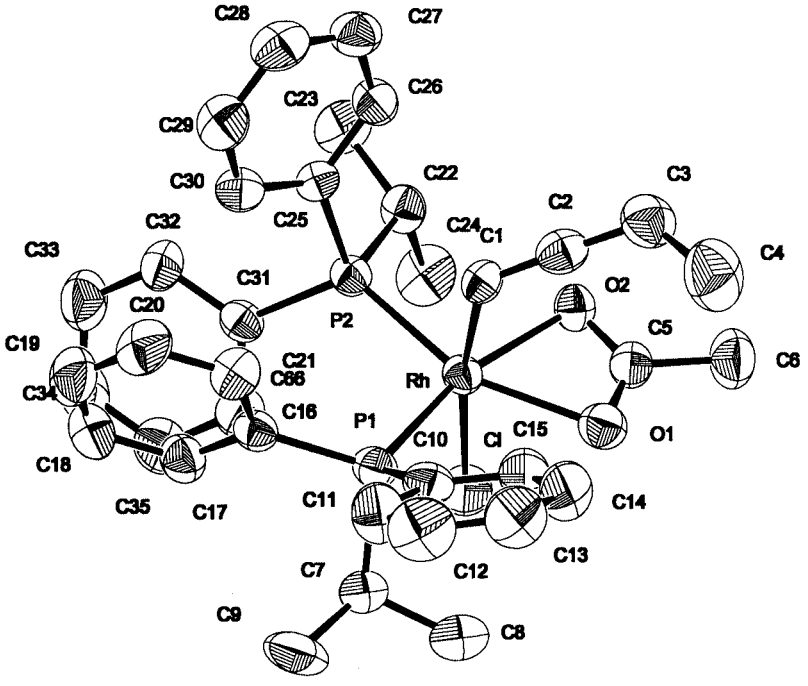
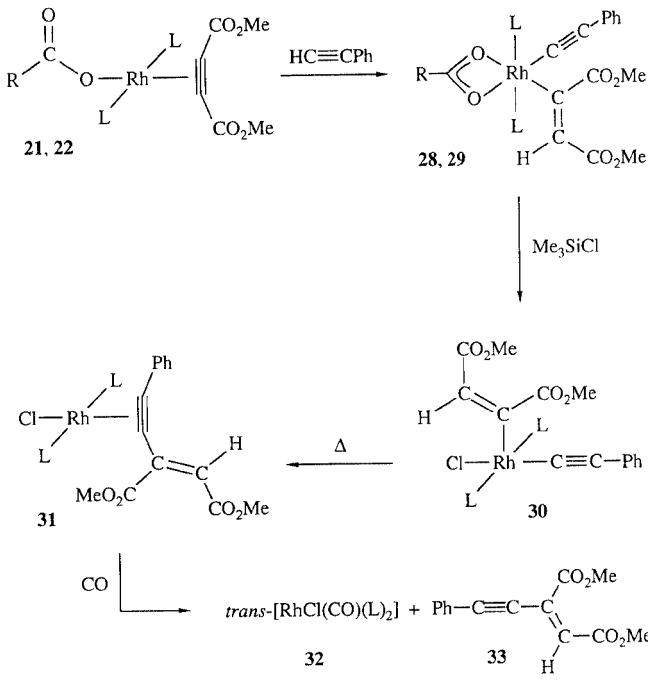


Figure 1. Molecular structure (ORTEP diagram) of **27**; selected bond lengths [Å] and angles [°]: Rh−P1 2.3050(17), Rh−P2 2.2910(19), Rh−O1 2.178(4), Rh−O2 2.135(3), Rh−Cl 2.4686(15), Rh−C1 2.051(5), C1−C2 1.263(7), C2−C3 1.336(8), C3−C4 1.475(9), O1−C5 1.255(6), O2−C5 1.264(6); P1−Rh−P2 100.61(6), P1−Rh−O1 103.41(11), P2−Rh−O1 155.78(10), P1−Rh−O2 163.94(12), P2−Rh−O2 95.11(12), P1−Rh−Cl 96.30(5), P2−Rh−Cl 98.12(5), P1−Rh−C1 87.73(15), P2−Rh−C1 89.08(15), Cl−Rh−C1 170.93(16), Cl−Rh−O1 82.35(11), Cl−Rh−O2 84.62(10), O1−Rh−C1 88.81(18), O2−Rh−C1 89.27(18), O1−Rh−O2 60.74(14), Rh−C1−C2 120.8(4), C1−C2−C3 177.0(6), C2−C3−C4 122.8(6)



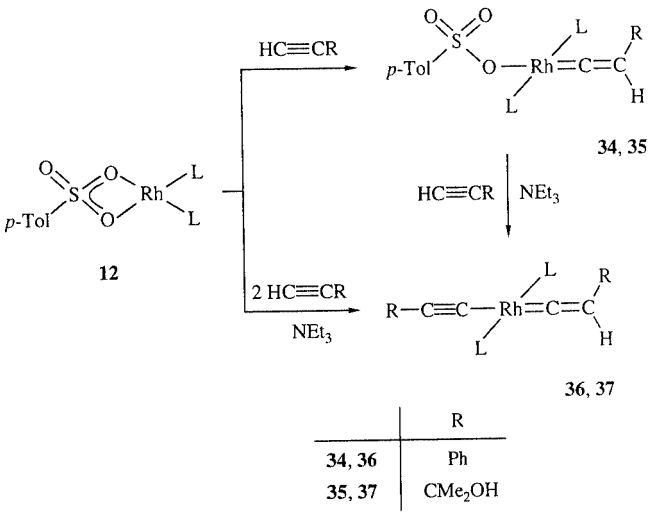
Scheme 8. (L = P*i*PrPh$_2$)

the chemical shift of the resonance of the vinylic proton in the ^{1}H NMR spectra, which is observed at δ = 6.00 (for **28**) and 6.04 (for **29**) and thus at higher field than in the case of a *trans*-position of H to rhodium.[3,16,21] The ^{13}C NMR spectroscopic data for the alkynyl and vinyl carbon atoms of **29** are quite similar to those of the structurally related compounds **24**−**26** and thus in agreement with the proposed structure. Regarding the course of the reaction of **21** and **22** with phenylacetylene, we assume that a similar mechanism is operative as suggested for the formation of **24** and **26**. Treatment of the square-planar starting materials **21** and **22** with HC≡CPh could lead via oxidative addition to a six-coordinate alkyne(alkynyl)hydridorhodium(III) species (see intermediate **B** in Scheme 7), which, after insertion of the alkyne RC≡CR into the Rh−H bond and concomitant closing of the chelate ring of the acetate, gives the products.

The alkynyl(vinyl) complexes **28** and **29** are thermally quite stable and even in the presence of CO do not react by intramolecular C−C coupling to yield *trans*-[Rh(κ^1-O$_2$CR)(CO)(P*i*PrPh$_2$)$_2$] and the enyne. Such a reductive elimination occurs if the related bis(triisopropylphosphane) compound [Rh(κ^2-O$_2$CCH$_3$)(C≡CCO$_2$Me){(*E*)-CH=CHCO$_2$Me}(P*i*Pr$_3$)$_2$] is stirred in benzene under a CO atmosphere at 80 °C.[12] However, if a solution of **28** or **29** in acetone is treated at −20 °C with an equimolar amount of Me$_3$SiCl, a fast reaction (illustrated by a quick change of color from pale-yellow to red) takes place and the five-coordinate chlororhodium(III) complex **30** is formed, along with the corresponding silyl ester RCO$_2$SiMe$_3$ (R = Me, *t*Bu; Scheme 8). While the signal for the vinylic proton in the ^{1}H NMR spectrum of **30** appears at practically the same position (δ = 6.04) as for the precursors **28** and **29**, the doublet resonance for the equivalent phosphorus atoms is observed in the ^{31}P NMR spectrum of **30** at δ = 18.9 and thus shifted upfield by 12−15 ppm from **28** and **29**. The change of the coordination number at rhodium could be responsible for this result. Although precise structural data for **30** (which is a red air-sensitive oil) are missing, we assume that the coordination geometry corresponds to a square pyramid with the vinyl group in the apical position, in analogy to [RhCl(C≡CPh){(*Z*)-CH=CHPh}(P*i*Pr$_3$)$_2$].[3]

The rearrangement of **30** to **31** by C−C coupling occurs smoothly and selectively in benzene at 60 °C and affords the enyne complex **31** as an orange, relatively air-stable solid in 75% isolated yield. The assumption that the enyne is coordinated through the triple bond is mainly supported by the IR spectrum, which shows the ν(C≡C) stretching mode at 1835 cm^{-1}, i.e. in a similar region as found for *trans*-[RhCl(η^2-PhC≡CPh)(P*i*Pr$_3$)$_2$].[22] Passing a slow stream of CO through a solution of **31** in CH$_2$Cl$_2$ at room temperature results in a displacement of the enyne by CO and leads to the carbonylrhodium(I) compound **32** and the free enyne **33**. The latter has been identified by comparison of its spectroscopic data with those from the literature.[23] As anticipated, **32** is also accessible from the dimer **3** and CO in virtually quantitative yield.

In contrast to the carboxylato derivatives **8** and **9**, the sulfonate **12** reacts with terminal alkynes HC≡CR (R = Ph, CMe$_2$OH) to give the four-coordinate rhodium(I) vinylidene complexes **34** and **35** instead of alkynyl(vinyl)- or allenylrhodium(III) complexes (Scheme 9). The reactions of **12** with HC≡CPh and HC≡CCMe$_2$OH in a molar ratio of 1:1 were carried out in toluene at room temperature and afford compounds **34** and **35** as violet air-sensitive solids almost quantitatively. Although it is safe to assume that in the initial step of the reaction an η^2-alkynerhodium(I) species is generated, which then rearranges, possibly via an alkynyl(hydrido)rhodium(III) intermediate, to the isolated product,[24] we failed to detect such a species by NMR spectroscopy. In analogy to the carboxylato complexes *trans*-

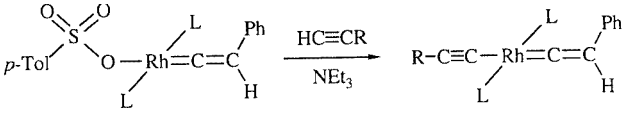


	R
34, 36	Ph
35, 37	CMe$_2$OH

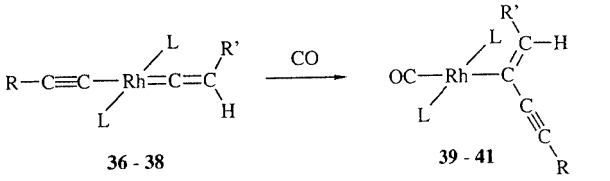
Scheme 9. (L = P*i*Pr$_2$Ph)

[Rh(κ^1-O$_2$CR)(=C=CHPh)(P*i*Pr$_3$)$_2$] (R = CH$_3$, CF$_3$),[11] the ^{13}C NMR spectra of **34** and **35** display two low-field resonances at δ = 306.9 and 113.4 (for **34**) and δ = 308.2 and 115.7 (for **35**) assigned to the α- and β-carbon atoms of the vinylidene units.

The Rh−O bond in compounds **34** and **35** is quite labile and thus upon treatment of solutions of **34** or **35** in a 1:1 mixture of toluene and triethylamine with an equimolar amount of the corresponding alkyne HC≡CR at −50 °C a substitution of the tosylate by the alkynyl anion takes place. After warming to room temperature, removal of the solvent and extraction of the residue with ether the alkynyl(vinylidene) complexes **36** and **37** are isolated in 56−68% yield. These compounds, which are turquoise or dark-green solids, can also be obtained directly from **12** and a twofold excess of HC≡CR under similar conditions; in this case, however, the yield is only 34−45%. Compounds **36** and **37** are less stable in solution than the triisopropylphosphane derivatives *trans*-[Rh(C≡CR)(=C=CHR)(P*i*Pr$_3$)$_2$],[3] which could be due to a reduced shielding of the metal center by the smaller P*i*Pr$_2$Ph ligands. The alkynyl(vinylidene) compound **38**, with different substituents at the β-C atom of the carbon-bonded units, is accessible from **34** and the alkynol HC≡CCMe$_2$OH (see Scheme 10); it is significantly more air-sensitive than the counterparts **36** and **37**. Attempts to prepare the isomer of **38** with the composition *trans*-[Rh(C≡CPh)(=C=CHCMe$_2$OH)(P*i*Pr$_2$Ph)$_2$] failed. Treatment of a solution of **35** in toluene/NEt$_3$ with one equiv. of phenylacetylene affords a mixture of products which could not be separated by fractional crystallization or chromatographic techniques.



34 **38**



36 - 38 **39 - 41**

	R	R'
36, 39	Ph	Ph
37, 40	CMe$_2$OH	CMe$_2$OH
38, 41	CMe$_2$OH	Ph

Scheme 10. (L = P*i*Pr$_2$Ph)

The alkynyl(vinylidene) complexes **36**−**38** react quite rapidly with CO in dichloromethane at −20 °C to give exclusively the (*Z*) isomers of the enynylrhodium(I) compounds **39**−**41** in moderate to good yields (see Scheme 10). We assume that initially CO adds to the metal center, thus generating a five-coordinate 18-electron intermediate, which, after migration of the alkynyl ligand to the α-carbon atom of the vinylidene unit, transforms into the isolated product. The importance of steric factors probably explains why the attack of the alkynyl moiety occurs only at that side of the molecule that is opposite to the substituent R′. Compounds **39**−**41** are less air-sensitive than the precursors **36**−**38** both in the solid state and in solution. Typical spectroscopic data of **39**−**41** are the intense ν(CO) and ν(C≡C) stretching modes in the IR spectra at 1950−1955 cm^{-1} and 2070−2160 cm^{-1}, respectively, and the resonance for the vinylic =CH proton in the ^{1}H NMR spectra at δ = 8.07 (**39**), 7.18 (**40**) and 7.20 (**41**). The latter is split into a doublet of triplets due to ^{1}H-^{103}Rh and ^{1}H-^{31}P coupling. It should also be mentioned that the methyl groups of the P*i*Pr$_2$Ph ligands of **39**−**41** are diastereotopic and give rise to four doublets of virtual triplets in the ^{1}H NMR spectra. We interpret this observation by assuming a hindered rotation of the vinylic unit around the Rh−C σ-bond, probably caused by the steric requirements of the substituents at the phosphorus atoms and the C=C bond.

In conclusion, the work described in this paper illustrates that a series of rhodium(I) and rhodium(III) complexes with [Rh(P*i*Pr$_2$Ph)$_2$] and [Rh(P*i*PrPh$_2$)$_2$] as molecular building blocks is accessible starting from the π-allylrhodium(I) compounds **4** and **5**. Protolytic cleavage of the allyl-metal bond by carboxylic acids or *p*-toluenesulfonic acid leads to the formation of carboxylato- and tosylatorhodium(I) derivatives, which easily undergo both addition and oxidative addition reactions. With terminal alkynes as substrates, either alkynyl(vinyl)- or allenylrhodium(III) complexes were obtained. Provided that C≡CPh is the alkynyl and C(CO$_2$Me)=CH(CO$_2$Me) the vinyl ligand, the alkynyl(vinyl) complexes react with Me$_3$SiCl by intramolecular C−C coupling to give enynerhodium compounds from which the free enyne is generated upon treatment with CO. The alkynyl(vinylidene)rhodium(I) derivatives, which were prepared in a stepwise manner from rhodium tosylates and terminal alkynes, also react with CO by migratory insertion to afford stereoselectively four-coordinate enynylrhodium(I) complexes. Treatment of catalytic amounts of the pivalatorhodium compounds **9** or **25** with excess phenylacetylene leads to a dimerization of the alkyne and gives regioselectively the branched enyne CH$_2$=C(Ph)−C≡CPh.

Experimental Section

General: All operations were carried out under argon using Schlenk techniques. The starting materials **1**[25] and PH*i*Pr$_2$ [26] were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC 200, Bruker AMX 400 and JEOL FX 90 Q instruments, unless otherwise stated. Abbreviations used: s, singlet; d, doublet; t, triplet; m, multiplet; vt, virtual triplet; br, broadened signal; $N = {}^2J_{P,H} + {}^3J_{P,H}$ or ${}^2J_{P,C} + {}^4J_{P,C}$. The assignment of protons for the π-allyl ligand in compounds **4**−**7** is as follows: H$_m$ = proton at central carbon atom; H$_s$ = proton of terminal CH$_2$ groups in *syn* position to H$_m$; H$_a$ = proton of ter-

minal CH_2 groups in *anti* position to H_m. Melting and decomposition points were measured by differential thermal analysis (DTA).

Preparation of [RhCl(P*i*Pr$_2$Ph)$_2$]$_2$ (2): A suspension of **1** (250 mg, 0.35 mmol) in toluene (20 mL) was treated with P*i*Pr$_2$Ph (0.29 mL, 1.40 mmol) and stirred for 10 min at room temperature. The solvent was evaporated in vacuo, the remaining violet solid was washed three times with 5-mL portions of pentane and dried; yield 360 mg (98%); m.p. 105 °C (dec.). ^{1}H NMR (200 MHz, C_6D_6): δ = 7.37−6.79 (m, 20 H, C_6H_5), 2.28 (m, 8 H, PC*H*CH$_3$), 1.70, 1.11 (both m, 48 H, PCHC*H*$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 58.9 (d, $^1J_{Rh,P}$ = 197.7 Hz). $C_{48}H_{76}Cl_2P_4Rh_2$ (1053.8): calcd. C 54.71, H 7.27; found C 54.49, H 7.79.

Preparation of [RhCl(P*i*PrPh$_2$)$_2$]$_2$ (3): This compound was prepared as described for **2**, with **1** (250 mg, 0.35 mmol) and P*i*PrPh$_2$ (0.32 mL, 1.40 mmol) as starting materials. Violet solid; yield 394 mg (95%); m.p. 98 °C (dec.). ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 7.36−7.06 (m, 40 H, C_6H_5), 2.22 (m, 4 H, PC*H*CH$_3$), 0.92 (dd, $^3J_{P,H}$ = 14.4, $^3J_{H,H}$ = 6.9 Hz, 12 H, PCHC*H*$_3$). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ = 55.2 (d, $^1J_{Rh,P}$ = 197.6 Hz). $C_{60}H_{68}Cl_2P_4Rh_2$ (1189.8): calcd. C 60.57, H 5.76; found C 60.08, H 5.81.

Preparation of [Rh(η^3-C$_3$H$_5$)(P*i*Pr$_2$Ph)$_2$] (4): A suspension of **1** (574 mg, 0.80 mmol) in toluene (5 mL) was treated with P*i*Pr$_2$Ph (0.66 mL, 3.20 mmol) and stirred for 10 min at room temperature. After cooling the solution to 0 °C, a 0.5 M solution of C_3H_5MgBr in ether (3.2 mL, 1.60 mmol) was added dropwise. A change of color from brown-violet to yellow occurred. The solvent was evaporated in vacuo, the residue was extracted with pentane (30 mL) and the extract was dried in vacuo. A yellow air-sensitive solid was obtained which was washed three times with 2-mL portions of acetone (0 °C) and dried; yield 700 mg (82%); m.p. 77 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6): δ = 7.41−6.83 (m, 10 H, C_6H_5), 5.02 (dtt, $^2J_{Rh,H}$ = 2.1, $^3J_{H,Ha}$ = 12.8, $^3J_{H,Hs}$ = 6.8 Hz, 1 H, H_m), 3.36 (d, $^3J_{H,Hm}$ = 6.8 Hz, 2 H, H_s), 2.49, 2.37 (both m, 4 H, PC*H*CH$_3$), 2.35 (dd, $^3J_{H,Hm}$ = 12.8, $^3J_{P,H}$ = 7.0 Hz, 2 H, H_a), 1.10 (dd, $^3J_{P,H}$ = 15.0, $^3J_{H,H}$ = 7.0 Hz, 6 H, PCHC*H*$_3$), 1.08 (dd, $^3J_{P,H}$ = 14.4, $^3J_{H,H}$ = 7.0 Hz, 6 H, PCHC*H*$_3$), 0.99 (dd, $^3J_{P,H}$ = 12.4, $^3J_{H,H}$ = 6.6 Hz, 6 H, PCHC*H*$_3$), 0.90 (dd, $^3J_{P,H}$ = 12.0, $^3J_{H,H}$ = 6.8 Hz, 6 H, PCHC*H*$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 53.2 (d, $^1J_{Rh,P}$ = 196.2 Hz). $C_{27}H_{43}P_2Rh$ (532.5): calcd. C 60.90, H 8.14; found C 60.23; H. 8.01.

Preparation of [Rh(η^3-C$_3$H$_5$)(P*i*PrPh$_2$)$_2$] (5): This compound was prepared as described for **4**, with **1** (287 mg, 0.40 mmol), P*i*PrPh$_2$ (0.37 mL, 1.60 mmol) and a 0.5 M solution of C_3H_5MgBr in ether (1.6 mL, 0.80 mmol) as starting materials. Yellow air-sensitive solid; yield 384 mg (80%); m.p. 76 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6): δ = 7.45−7.02 (m, 20 H, C_6H_5), 5.08 (dtt, $^2J_{Rh,H}$ = 2.1, $^3J_{H,Ha}$ = 12.2, $^3J_{H,Hs}$ = 6.8 Hz, 1 H, H_m), 3.31 (d, $^3J_{H,Hm}$ = 6.8 Hz, 2 H, H_s), 2.37 (dd, $^3J_{H,Hm}$ = 12.2, $^3J_{P,H}$ = 4.7 Hz, 2 H, H_a), 2.15 (m, 2 H, PC*H*CH$_3$), 0.99 (dd, $^3J_{P,H}$ = 14.7, $^3J_{H,H}$ = 6.9 Hz, 6 H, PCHC*H*$_3$), 0.91 (dd, $^3J_{P,H}$ = 14.4, $^3J_{H,H}$ = 7.0 Hz, 6 H, PCHC*H*$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ = 49.9 (d, $^1J_{Rh,P}$ = 197.3 Hz). $C_{33}H_{39}P_2Rh$ (600.5): calcd. C 66.00, H 6.55; found C 65.90, H 6.56.

Preparation of [Rh(η^3-C$_3$H$_5$)(PH*i*Pr$_2$)$_2$] (6): This compound was prepared as described for **4**, with **1** (287 mg, 0.40 mmol), PH*i*Pr$_2$ (0.24 mL, 1.60 mmol) and a 0.5 M solution of C_3H_5MgBr in ether (1.6 mL, 0.80 mmol) as starting materials. Yellow air-sensitive solid; yield 253 mg (83%); m.p. 65 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6): δ = 4.82 (dtt, $^2J_{Rh,H}$ = 1.9, $^3J_{H,Ha}$ = 12.7, $^3J_{H,Hs}$ = 7.2 Hz, 1 H, H_m), 4.06 (dt, $^1J_{P,H}$ = 256.5, $^3J_{H,H}$ = 4.8 Hz, 2 H, PH), 3.68 (d, $^3J_{H,Hm}$ = 7.2 Hz, 2 H, H_s), 2.22 (dd, $^3J_{H,Hm}$ = 12.7, $^3J_{P,H}$ = 5.9 Hz, 2 H, H_a), 2.01, 1.93 (both m, 4 H, PC*H*CH$_3$), 1.13 (dd, $^3J_{P,H}$ = 13.5, $^3J_{H,H}$ = 6.8 Hz, 6 H, PCHC*H*$_3$), 1.11 (dd, $^3J_{P,H}$ = 16.2, $^3J_{H,H}$ = 7.2 Hz, 6 H, PCHC*H*$_3$), 1.04 (dd, $^3J_{P,H}$ = 13.8, $^3J_{H,H}$ = 6.9 Hz, 6 H, PCHC*H*$_3$), 1.02 (dd, $^3J_{P,H}$ = 16.5, $^3J_{H,H}$ = 7.1 Hz, 6 H, PCHC*H*$_3$). ^{31}P NMR (36.2 MHz, C_6D_6): δ = 56.5 (d, $^1J_{Rh,P}$ = 187.6 Hz). $C_{15}H_{35}P_2Rh$ (380.3): calcd. C 47.38, H 9.28; found C 47.23; H 9.35.

Preparation of [Rh(η^3-C$_3$H$_5$)(P*t*Bu$_2$Me)$_2$] (7): This compound was prepared as described for **4**, with **1** (287 mg, 0.40 mmol), P*t*Bu$_2$Me (0.32 mL, 1.60 mmol) and a 0.5 M solution of C_3H_5MgBr in ether (1.6 mL, 0.80 mmol) as starting materials. Yellow air-sensitive solid; yield 320 mg (86%); m.p. 86 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6): δ = 4.63 (dtt, $^2J_{Rh,H}$ = 2.1, $^3J_{H,Ha}$ = 11.7, $^3J_{H,Hs}$ = 6.7 Hz, 1 H, H_m), 3.74 (d, $^3J_{H,Hm}$ = 6.7 Hz, 2 H, H_s), 1.92 (dd, $^3J_{H,Hm}$ = 11.7, $^3J_{P,H}$ = 6.1 Hz, 2 H, H_a), 1.22 (d, $^3J_{P,H}$ = 12.0 Hz, 18 H, PCCH$_3$), 1.14 (d, $^2J_{P,H}$ = 4.3 Hz, 6 H, PCH$_3$), 1.11 (d, $^3J_{P,H}$ = 11.6 Hz, 18 H, PCCH$_3$). ^{31}P NMR (36.2 MHz, C_6D_6): δ = 53.3 (d, $^1J_{Rh,P}$ = 196.4 Hz). $C_{21}H_{47}P_2Rh$ (464.5): calcd. C 54.31, H 10.20; found C 54.82, H 10.32.

Preparation of [Rh(κ^2-O$_2$CCH$_3$)(P*i*PrPh$_2$)$_2$] (8): A solution of **5** (180 mg, 0.30 mmol) in benzene (2 mL) was treated with acetic acid (17 μL, 0.30 mmol) and stirred for 1 h at room temperature. A change of color from yellow to dark red occurred. The solvent was evaporated in vacuo, the residue was extracted with acetone (20 mL) and the extract was concentrated to ca. 3 mL in vacuo. A dark-red microcrystalline solid was obtained, which was filtered, washed twice with 2-mL portions of acetone (0 °C) and dried; yield 165 mg (89%); m.p. 108 °C. IR (C_6H_6): ν(OCO$_{as}$) = 1510, ν(OCO$_{sym}$) = 1445 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.83−6.69 (m, 20 H, C_6H_5), 2.32 (m, 2 H, PC*H*CH$_3$), 1.95 (s, 3 H, O_2CCH_3), 1.10 (m, 12 H, PCHC*H*$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ = 61.9 (d, $^1J_{Rh,P}$ = 199.7 Hz). $C_{32}H_{37}O_2P_2Rh$ (618.5): calcd. C 62.14, H 6.03; found C 61.75, H 5.98.

Preparation of [Rh{κ^2-O$_2$CC(CH$_3$)$_3$}(P*i*PrPh$_2$)$_2$] (9): This compound was prepared as described for **8**, with **5** (150 mg, 0.25 mmol) and $(CH_3)_3CCO_2H$ (26 μL, 0.25 mmol) as starting materials; reaction time: 6 h. Dark-red solid; yield 129 mg (78%); m.p. 93 °C (dec.). IR (KBr): ν(OCO$_{as}$) = 1485, ν(OCO$_{sym}$) = 1430 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.52−6.81 (m, 20 H, C_6H_5), 2.37 (m, 2 H, PC*H*CH$_3$), 1.34 [s, 9 H, C(CH$_3$)$_3$], 1.02 (m, 12 H, PCHC*H*$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ = 62.2 (d, $^1J_{Rh,P}$ = 226.0 Hz). $C_{35}H_{43}O_2P_2Rh$ (660.9): calcd. C 63.64, H 6.56; found C 64.03, H 6.81.

Preparation of [Rh{κ^2-O$_2$CC(CH$_3$)$_3$}(P*i*Pr$_2$Ph)$_2$] (10): This compound was prepared as described for **8**, with **4** (149 mg, 0.28 mmol) and $(CH_3)_3CCO_2H$ (29 μL, 0.28 mmol) as starting materials; reaction time: 6 h. Dark-red solid; yield 123 mg (74%); m.p. 97 °C (dec.). IR (C_6H_6): ν(OCO$_{as}$) = 1480, ν(OCO$_{sym}$) = 1425 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.58−6.91 (m, 10 H, C_6H_5), 2.25 (m, 4 H, PC*H*CH$_3$), 1.53 (m, 12 H, PCHC*H*$_3$), 1.42 [s, 9 H, C(CH$_3$)$_3$], 1.15 (m, 12 H, PCHC*H*$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 66.6 (d, $^1J_{Rh,P}$ = 202.1 Hz). $C_{29}H_{47}O_2P_2Rh$ (592.6): calcd. C 58.78, H 7.99; found C 58.51, H 8.02.

Preparation of [Rh{κ^2-O$_2$S(O)-*p*-Tol}(P*i*PrPh$_2$)$_2$] (11): A solution of **5** (180 mg, 0.30 mmol) in toluene (2 mL) was treated with 4-MeC$_6$H$_4$SO$_3$H (57 mg, 0.30 mmol) and stirred for 1 h at room temperature. A change of color from yellow to red occurred. The solvent was evaporated in vacuo, the residue was extracted with acetone (20 mL) and the extract was concentrated to ca. 2 mL in vacuo. Red crystals precipitated which were filtered, washed twice with 2-mL portions of acetone (0 °C) and dried; yield 185 mg (89%); m.p.

51 °C. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.58−6.91 (m, 24 H, C_6H_4 and C_6H_5), 2.31 (m, 2 H, PC*H*CH$_3$), 1.95 (s, 3 H, $C_6H_4CH_3$), 0.96 (m, 12 H, PCHC*H*$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 63.3 (d, $^1J_{Rh,P}$ = 212.2 Hz). $C_{37}H_{41}O_3P_2RhS$ (730.7): calcd. C 60.82, H 5.66, S 4.39; found C 60.82, H 5.89, S 4.33.

Preparation of [Rh{κ^2-O$_2$S(O)-*p*-Tol}(P*i*Pr$_2$Ph)$_2$] (12): This compound was prepared as described for **11**, with **4** (128 mg, 0.24 mmol) and 4-Me$C_6H_4SO_3H$ (46 mg, 0.24 mmol) as starting materials. Red air-sensitive crystals; yield 138 mg (87%); m.p. 85 °C (dec.). ^{1}H NMR (200 MHz, C_6D_6): δ = 8.46−6.79 (m, 14 H, C_6H_4 and C_6H_5), 2.10 (m, 4 H, PC*H*CH$_3$), 1.97 (s, 3 H, $C_6H_4CH_3$), 1.35, 1.03 (both m, 12 H each, PCHC*H*$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 63.3 (d, $^1J_{Rh,P}$ = 212.2 Hz). $C_{31}H_{45}O_3P_2RhS$ (662.6): calcd. C 56.19, H 6.84, S 4.84; found C 55.82, H 6.53, S 4.71.

Preparation of *trans*-[Rh(κ^1-O$_2$CCH$_3$)(CO)(P*i*PrPh$_2$)$_2$] (13): A slow stream of CO was passed through a solution of **8** (62 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) at room temperature for 10 s, leading to a rapid change of color from dark-red to light yellow. After removal of the solvent in vacuo, a light yellow solid was obtained, which was washed twice with 2-mL portions of acetone (0 °C) and dried; yield (98%); m.p. 135 °C. IR (KBr): ν(CO) = 1960, ν(OCO_{as}) = 1595, ν(OCO_{sym}) = 1370 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.83−7.41 (m, 20 H, C_6H_5), 2.93 (m, 2 H, PC*H*CH$_3$), 1.36 (s, 3 H, O_2CCH_3), 1.21 (dvt, *N* = 15.8, $^3J_{H,H}$ = 7.4 Hz, 12 H, PCHC*H*$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ = 40.7 (d, $^1J_{Rh,P}$ = 147.4 Hz). $C_{33}H_{37}O_3P_2Rh$ (646.5): calcd. C 61.31, H 5.77; found C 61.00, H 5.30.

Preparation of *trans*-[Rh{κ^1-O$_2$CC(CH$_3$)$_3$}(CO)(P*i*Pr$_2$Ph)$_2$] (14): This compound was prepared as described for **13**, with **10** (59 mg, 0.10 mmol) and CO as starting materials. Yellow solid; yield 59 mg (95%); m.p. 93 °C (dec.). IR (KBr): ν(CO) = 1955 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.77−7.07 (m, 10 H, C_6H_5), 2.42 (m, 4 H, PC*H*CH$_3$), 1.37 (dvt, *N* = 16.1, $^3J_{H,H}$ = 7.3 Hz, 12 H, PCHC*H*$_3$), 1.14 [s, 9 H, C(CH$_3$)$_3$], 1.03 (dvt, *N* = 14.2, $^3J_{H,H}$ = 6.9 Hz, 12 H, PCHC*H*$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 46.4 (d, $^1J_{Rh,P}$ = 133.7 Hz). $C_{30}H_{47}O_3P_2Rh$ (620.6): calcd. C 58.07, H 7.63; found C 57.60, H 7.46.

Preparation of [Rh{κ^1-O$_2$S(O)-*p*-Tol}(CO)(P*i*Pr$_2$Ph)$_2$] (15): This compound was prepared as described for **13**, with **12** (66 mg, 0.10 mmol) and CO as starting materials. Yellow solid; yield 64 mg (93%); m.p. 153 °C (dec.). IR (KBr): ν(CO) = 1950 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.96−6.82 (m, 14 H, C_6H_5 and C_6H_4), 2.81 (m, 4 H, PC*H*CH$_3$), 1.95 (s, 3 H, $C_6H_4CH_3$) 1.44 (dvt, *N* = 16.9, $^3J_{H,H}$ = 7.5 Hz, 12 H, PCHC*H*$_3$), 0.96 (dvt, *N* = 14.5, $^3J_{H,H}$ = 7.0 Hz, 12 H, PCHC*H*$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 47.7 (d, $^1J_{Rh,P}$ = 125.0 Hz). $C_{32}H_{45}O_4P_2RhS$ (690.6): calcd. C 55.65; H 6.57; found C 56.07, H 6.81.

Preparation of [RhH$_2$(κ^2-O$_2$CCH$_3$)(P*i*PrPh$_2$)$_2$] (16): A slow stream of H_2 was passed through a solution of **8** (62 mg, 0.10 mmol) in CH_2Cl_2 (5 mL) at room temperature for 5 min. After removal of the solvent in vacuo, a white solid was obtained which was washed twice with 1-mL portions of acetone (0 °C) and dried; yield 56 mg (90%); m.p. 84 °C (dec.). IR (KBr): ν(RhH) = 2100, ν(OCO_{as}) = 1540, ν(OCO_{sym}) =1430 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.99−6.91 (m, 20 H, C_6H_5), 2.53 (m, 2 H, PC*H*CH$_3$), 1.52 (s, 3 H, O_2CCH_3), 1.21 (dvt, *N* = 15.9, $^3J_{H,H}$ = 8.0 Hz, 12 H, PCHC*H*$_3$), −22.01 (dt, $^1J_{Rh,H}$ = 22.4, $^2J_{P,H}$ = 18.0 Hz, 2 H, RhH). ^{31}P NMR (162.0 MHz, C_6D_6): δ = 49.7 (d, $^1J_{Rh,P}$ = 119.4 Hz). $C_{32}H_{39}O_2P_2Rh$ (620.5): calcd. C 61.94, H 6.33; found C 62.20, H 6.48.

Preparation of [RhH$_2${κ^2-O$_2$CC(CH$_3$)$_3$}(P*i*PrPh$_2$)$_2$] (17): This compound was prepared as described for **16**, with **9** (66 mg, 0.10 mmol) and H_2 as starting materials. White solid; yield 58 mg (88%); m.p. 76 °C (dec.). IR (KBr): ν(RhH) = 2115, ν(OCO_{as}) = 1525, ν(OCO_{sym}) = 1430 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 6.99−6.71 (m, 20 H, C_6H_5), 2.33 (m, 2 H, PC*H*CH$_3$), 1.08 (dvt, *N* = 16.7, $^3J_{H,H}$ = 8.0 Hz, 12 H, PCHC*H*$_3$), 0.79 [s, 9 H, C(CH$_3$)$_3$], −21.13 (dt, $^1J_{Rh,H}$ = 21.8, $^2J_{P,H}$ = 17.4 Hz, 2 H, RhH). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 49.8 (d, $^1J_{Rh,P}$ = 119.2 Hz). $C_{35}H_{45}O_2P_2Rh$ (662.6): calcd. C 63.45, H 6.85; found C 63.90, H 7.12.

Preparation of [RhH$_2${κ^2-O$_2$CC(CH$_3$)$_3$}(P*i*Pr$_2$Ph)$_2$] (18): This compound was prepared as described for **16**, with **10** (65 mg, 0.11 mmol) and H_2 as starting materials. Colorless oil; yield 65 mg (99%). IR (KBr): ν(RhH) = 2120, ν(OCO_{as}) = 1520, ν(OCO_{sym}) = 1420 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.88−6.92 (m, 10 H, C_6H_5), 2.26 (m, 4 H, PC*H*CH$_3$), 1.28 (dvt, *N* = 14.5, $^3J_{H,H}$ = 7.3 Hz, 12 H, PCHC*H*$_3$), 1.14 [s, 9 H, C(CH$_3$)$_3$], 1.02 (dvt, *N* = 13.1, $^3J_{H,H}$ = 7.3 Hz, 12 H, PCHC*H*$_3$), −22.73 (dt, $^1J_{Rh,H}$ = 23.3, $^2J_{P,H}$ = 16.0 Hz, 2 H, RhH). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 55.3 (d, $^1J_{Rh,P}$ = 119.1 Hz). $C_{29}H_{49}O_2P_2Rh$ (594.6): calcd. C 58.58, H 8.31; found C 58.45, H 8.28.

Preparation of [RhH$_2${κ^2-O$_2$S(O)-*p*-Tol}(P*i*PrPh$_2$)$_2$] (19): This compound was prepared as described for **16**, with **11** (73 mg, 0.10 mmol) and H_2 as starting materials. White solid which has to be stored under dihydrogen; yield 62 mg (85%); m.p. 86 °C (dec.). IR (KBr): ν(RhH) = 2100 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.87−6.49 (m, 24 H, C_6H_5 and C_6H_4), 3.08 (m, 2 H, PC*H*CH$_3$), 1.80 (s, 3 H, $C_6H_4CH_3$), 1.12 (dvt, *N* = 15.8, $^3J_{H,H}$ = 7.9 Hz, 12 H, PCHC*H*$_3$), −21.51 (dt, $^1J_{Rh,H}$ = 27.6, $^2J_{P,H}$ = 15.8 Hz, 2 H, RhH). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 50.2 (d, $^1J_{Rh,P}$ = 117.8 Hz). $C_{37}H_{43}O_3P_2RhS$ (732.7): calcd. C 60.66, H 5.92; found C 61.21, H 6.21.

Preparation of [RhH$_2${κ^2-O$_2$S(O)-*p*-Tol}(P*i*Pr$_2$Ph)$_2$] (20): This compound was prepared as described for **16**, with **12** (60 mg, 0.09 mmol) and H_2 as starting materials. Colorless oil which has to be stored under dihydrogen; yield 59 mg (98%). IR (KBr): ν(RhH) = 2130 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.81−6.65 (m, 14 H, C_6H_5 and C_6H_4), 2.52 (m, 4 H, PC*H*CH$_3$), 1.87 (s, 3 H, $C_6H_4CH_3$), 1.28 (dvt, *N* = 14.5, $^3J_{H,H}$ = 7.3 Hz, 12 H, PCHC*H*$_3$), 0.98 (dvt, *N* = 14.5, $^3J_{H,H}$ = 7.3 Hz, 12 H, PCHC*H*$_3$), −24.04 (dt, $^1J_{Rh,H}$ = 27.6, $^2J_{P,H}$ = 16.0 Hz, 2 H, RhH). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 51.8 (d, $^1J_{Rh,P}$ = 117.7 Hz). $C_{31}H_{47}O_3P_2RhS$ (664.6): calcd. C 56.02, H 7.13, S 4.82; found C 55.31, H 7.01, S 4.75.

Preparation of *trans*-[Rh(κ^1-O$_2$CCH$_3$){η^2-C$_2$(CO$_2$Me)$_2$}(P*i*PrPh$_2$)$_2$] (21): A solution of **8** (74 mg, 0.12 mmol) in benzene (5 mL) at room temperature was treated dropwise with $C_2(CO_2Me)_2$ (14 μL, 0.12 mmol) with continuous stirring. A quick change of color from dark-red to yellow occurred. The solvent was evaporated in vacuo and the oily residue dissolved in hexane (2 mL). After the solution was stored at −78 °C for 12 h, a pale-yellow solid precipitated, which was separated from the mother liquor, washed twice with 2-mL portions of pentane and dried in vacuo; yield: 78 mg (85%); m.p. 94 °C (dec.). IR (KBr): ν(C≡C) = 1810, ν(C=O) = 1680, ν(OCO) = 1610 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.81−7.00 (m, 20 H, C_6H_5), 3.24 (s, 6 H, CO_2CH_3), 2.68 (m, 2 H, PC*H*CH$_3$), 1.55 (dvt, *N* = 14.0, $^3J_{H,H}$ = 7.0 Hz, 12 H, PCHC*H*$_3$), 1.34 (s, 3 H, O_2CCH_3). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 34.6 (d, $^1J_{Rh,P}$ = 118.3 Hz). $C_{38}H_{43}O_6P_2Rh$ (760.6): calcd. C 60.01, H 5.70; found C 60.48, H 5.95.

Preparation of *trans*-[Rh{κ^1-O$_2$CC(CH$_3$)$_3$}{η^2-C$_2$(CO$_2$Me)$_2$}(P*i*PrPh$_2$)$_2$] (22): This compound was prepared as described for **21**,

with **9** (79 mg, 0.12 mmol) and $C_2(CO_2Me)_2$ (14 μL, 0.12 mmol). Pale-yellow solid; yield 79 mg (86%); m.p. 84 °C (dec.). IR (KBr): ν(C≡C) = 1785, ν(C=O) = 1685, ν(OCO_{as}) = 1610 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 7.85−6.98 (m, 20 H, C_6H_5), 3.32 (s, 6 H, CO_2CH_3), 2.64 (m, 2 H, PC*H*CH_3), 1.03 (dvt, *N* = 12.8, $^3J_{H,H}$ = 5.7 Hz, 12 H, PCHC*H*$_3$), 0.75 [s, 9 H, C(CH_3)$_3$]. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 35.9 (d, $^1J_{Rh,P}$ = 120.0 Hz). $C_{41}H_{49}O_6P_2Rh$ (802.7): calcd. C 61.35, H 6.15; found C 60.97, H 5.98.

Preparation of *trans*-[Rh{κ^1-$O_2CC(CH_3)_3$}(η^2-MeC≡CCO_2Me)(P*i*PrPh$_2$)$_2$] (23): A solution of **9** (92 mg, 0.14 mmol) in toluene (2 mL) was treated dropwise at −20 °C with MeC_2CO_2Me (14 μL, 0.14 mmol). After stirring the solution at −20 °C for 2 h and then warming to room temperature, the solvent was evaporated in vacuo. The oily residue was dissolved in hexane (2 mL) and the solution worked up as described for **21**. Pale-yellow solid; yield 67 mg (63%); m.p. 64 °C (dec.). IR (KBr): ν(C≡C) = 1900, ν(C=O) = 1705, ν(OCO_{as}) = 1670 cm^{-1}. ^1H NMR (200 MHz, [D_8]toluene, 243 K): δ = 7.92−6.84 (m, 20 H, C_6H_5), 3.33 (s, 3 H, CO_2CH_3), 2.38 (m, 2 H, PC*H*CH_3), 1.32 [s, 9 H, C(CH_3)$_3$], 1.30 (dvt, *N* = 17.3, $^3J_{H,H}$ = 8.6 Hz, 12 H, PCHC*H*$_3$), 1.10 (s, 3 H, ≡CCH_3). ^{31}P NMR (81.0 MHz, [D_8]toluene, 243 K): δ = 36.4 (d, $^1J_{Rh,P}$ = 123.5 Hz). $C_{40}H_{49}O_4P_2Rh$ (758.7):calcd. C 63.33, H 6.51; found C 63.45, H 6.55.

Preparation of [Rh(κ^2-O_2CCH_3)(C≡C*P*h){C(Ph)=CH_2}(P*i*PrPh$_2$)$_2$] (24): A solution of **8** (93 mg, 0.15 mmol) in toluene (5 mL) at −50 °C was treated dropwise with phenylacetylene (32 μL, 0.30 mmol). After stirring the solution for 5 min at −50 °C and then warming to room temperature, the solvent was evaporated in vacuo. The oily residue was dissolved in hexane (20 mL) and the solution stirred at 0 °C for 2 h. A pale-yellow solid slowly precipitated, which was filtered, washed twice with 2-mL portions of hexane and dried in vacuo; yield 106 mg (86%); m.p. 81 °C (dec.). IR (KBr): ν(C≡C) = 2060, ν(C=C) = 1580, ν(OCO_{as}) = 1520 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ = 8.04−6.46 (m, 30 H, C_6H_5), 5.87, 5.42 (both s, 1 H each, =CH_2), 3.35 (m, 2 H, PC*H*CH_3), 1.45 (dvt, *N* = 14.8, $^3J_{H,H}$ = 7.4 Hz, 6 H, PCHC*H*$_3$), 1.22 (dvt, *N* = 14.6, $^3J_{H,H}$ = 7.2 Hz, 6 H, PCHC*H*$_3$), 1.20 (s, 3 H, O_2CCH_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 182.2 (s, O_2C), 148.4 [dt, $^1J_{Rh,C}$ = 30.4, $^2J_{P,C}$ = 8.9 Hz, Rh*C*(=CH_2)Ph], 134.2−124.0 (m, C_6H_5), 128.6 [dt, $^2J_{Rh,C}$ = 1.2, $^3J_{P,C}$ = 0.8 Hz, =CH_2], 108.7 (dt, $^2J_{Rh,C}$ = 10.2, $^3J_{P,C}$ = 2.3 Hz, ≡*C*Ph], 98.5 [dt, $^1J_{Rh,C}$ = 50.7, $^2J_{P,C}$ = 18.5 Hz, Rh*C*≡CPh], 25.6 (vt, *N* = 25.3 Hz, P*C*HCH$_3$), 22.9 (s, O_2CCH_3), 18.2, 17.4 (both s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 31.0 (d, $^1J_{Rh,P}$ = 106.1 Hz). $C_{48}H_{49}O_2P_2Rh$ (822.8): calcd. C 70.07, H 6.00; found C 69.72, H 6.14.

Preparation of [Rh{κ^2-$O_2CC(CH_3)_3$}(C≡C*P*h){C(Ph)=CH_2}(P*i*PrPh$_2$)$_2$] (25): This compound was prepared as described for **24**, with **9** (99 mg, 0.15 mmol) and phenylacetylene (32 μL, 0.30 mmol) as starting materials. Pale-yellow solid; yield 109 mg (84%); m.p. 78 °C (dec.). IR (KBr): ν(C≡C) = 2050, ν(C=C) = 1580, ν(OCO_{as}) = 1485, ν(OCO_{sym}) = 1435 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 8.02−6.83 (m, 30 H, C_6H_5), 5.96, 5.49 (both s, 1 H each, =CH_2), 3.54 (m, 2 H, PC*H*CH_3), 1.52 (dvt, *N* = 10.2, $^3J_{H,H}$ = 7.1 Hz, 6 H, PCHC*H*$_3$), 1.08 (dvt, *N* = 14.8, $^3J_{H,H}$ = 7.5 Hz, 6 H, PCHC*H*$_3$), 1.73 [s, 9 H, C(CH_3)$_3$]. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 190.3 (s, O_2C), 150.5 [dt, $^1J_{Rh,C}$ = 28.7, $^2J_{P,C}$ = 18.5 Hz, Rh*C*(=CH_2)Ph], 135.5−125.4 (m, C_6H_5), 125.7 (dt, $^2J_{Rh,C}$ = 4.4, $^3J_{P,C}$ = 5.1 Hz, =CH_2), 109.3 (dt, $^2J_{Rh,C}$ = 8.7, $^3J_{P,C}$ = 4.7 Hz, ≡*C*Ph), 99.9 (dt, $^1J_{Rh,C}$ = 50.1, $^2J_{P,H}$ = 18.5 Hz, Rh*C*≡CPh), 39.4 [s, *C*(CH_3)$_3$], 27.1 [s, C(*C*H$_3$)$_3$], 26.4 (vt, *N* = 25.4 Hz, P*C*HCH$_3$), 19.3, 19.0 (both s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 29.5 (d, $^1J_{Rh,P}$ = 104.6 Hz). MS (70 eV, e-spray): *m/z* = 864 [M^+]. $C_{51}H_{55}O_2P_2Rh$ (864.9): calcd. C 70.83, H 6.41; found C 70.79, H 6.40.

Catalytic Dimerization of Phenylacetylene: A solution of either **9** (165 mg, 0.25 mmol) or **25** (260 mg, 0.25 mmol) in benzene (25 mL) was treated with phenylacetylene (2.7 mL, 25 mmol) and hexane (1 mL, as a reference for GC) and stirred whilst irradiating with an Osram 500 W lamp (λ = 300 nm) at room temperature. After 6 h, the GC plot (measured with a Shimadzu GC-8A gas chromatograph and a FFAP column) revealed that 80% of phenylacetylene had been consumed. The volatiles were removed in vacuo and the remaining red-brown oil investigated by ^1H NMR spectroscopy. The ^1H NMR spectrum showed that the major product was the enyne PhC≡CC(Ph)=CH_2, whereas the isomeric butenynes (*E*)- and (*Z*)-PhC≡CCH=CHPh were present in less than 1%. The red-brown oil was dissolved in benzene (2 mL) and the solution chromatographed on Al_2O_3 (neutral, activity grade I, height of column 15 cm). A yellow fraction was eluted with hexane, which was then dried in vacuo. The yellow oil (which slowly polymerizes at temperatures above −40 °C) was identified as PhC≡CC(Ph)=CH_2 by comparison of its NMR spectroscopic data with those of the literature.[27]

Preparation of [Rh(κ^2-O_2CCH_3)(C≡CCO_2Me){(*E*)-CH=$CHCO_2Me$}(P*i*PrPh$_2$)$_2$] (26): This compound was prepared as described for **24**, with **8** (74 mg, 0.12 mmol) and methyl propiolate (22 μL, 0.24 mmol) as starting materials. Pale-yellow solid; yield 83 mg (88%); m.p. 132 °C (dec.). IR (KBr): ν(C≡C) = 2090, ν(C=O) = 1675, ν(OCO_{as}) = 1570 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 9.18 (ddt, $^3J_{H,H}$ = 14.6, $^3J_{P,H}$ = 2.9, $^2J_{Rh,H}$ = 0.9 Hz, 1 H, RhCH), 7.77−6.95 (m, 20 H, C_6H_5), 6.33 (ddt, $^3J_{H,H}$ = 14.6, $^4J_{P,H}$ = 1.5, $^3J_{Rh,H}$ = 1.5 Hz, 1 H, =C*H*CO_2CH_3), 3.38, 3.36 (both s, 6 H, CO_2CH_3), 3.06 (m, 2 H, PC*H*CH_3), 1.30 (dvt, *N* = 15.7, $^3J_{H,H}$ = 7.3 Hz, 6 H, PCHC*H*$_3$), 1.06 (dvt, *N* = 15.0, $^3J_{H,H}$ = 7.3 Hz, 6 H, PCHC*H*$_3$), 1.05 (s, 3 H, O_2CCH_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 184.7 (s, RhO_2CCH_3), 168.0 (dt, $^1J_{Rh,C}$ = 29.3, $^2J_{P,C}$ = 9.8 Hz, RhCH), 162.7 (dt, $^3J_{Rh,C}$ = 2.7, $^4J_{P,C}$ = 1.3 Hz, CCO_2CH_3), 153.7 (dt, $^3J_{Rh,C}$ = 1.6, $^4J_{P,C}$ = 1.3 Hz, *C*O_2CH_3), 135.2, 134.7 (both vt, *N* = 9.8 Hz, *ortho*-C of C_6H_5), 130.3, 130.2 (both s, *para*-C of C_6H_5), 129.2, 129.2 (both vt, *N* = 41.8 Hz, *ipso*-C of C_6H_5), 128.0, 127.9 (both vt, *N* = 9.4 Hz, *meta*-C of C_6H_5), 127.5 (dt, $^2J_{Rh,C}$ = 9.3, $^3J_{P,C}$ = 4.5 Hz, =*C*HCO_2CH_3), 109.1 (dt, $^1J_{Rh,C}$ = 50.5, $^2J_{P,C}$ = 17.1 Hz, Rh*C*≡C), 103.6 (dt, $^2J_{Rh,C}$ = 11.0, $^3J_{P,C}$ = 2.4 Hz, RhC≡*C*), 50.4, 50.1 (both s, CO_2CH_3), 26.9 (vt, *N* = 26.5 Hz, P*C*HCH$_3$), 23.9 (s, O_2CCH_3), 18.9, 18.8 (both s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 33.6 (d, $^1J_{Rh,P}$ = 98.8 Hz). $C_{40}H_{45}O_6P_2Rh$ (786.7): calcd. C 61.07, H 5.77; found C 60.71, H 5.43.

Preparation of [RhCl(κ^2-O_2CCH_3)(CH=C=CHMe)(P*i*PrPh$_2$)$_2$] (27): A solution of **8** (93 mg, 0.15 mmol) in CH_2Cl_2 (5 mL) was treated at −20 °C with 3-chloro-1-butyne (13 μL, 0.15 mmol), leading to a rapid change of color from dark-red to yellow. After warming the solution to room temperature, the solvent was evaporated in vacuo. A yellow solid was obtained which was washed twice with 1-mL portions of acetone (0 °C) and dried; yield 93 mg (88%); m.p. 124 °C (dec.). IR (KBr): ν(OCO_{as}) = 1460 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ = 7.88−6.75 (m, 20 H, C_6H_5), 4.96 (dq, $^3J_{H,H}$ = 6.8, $^4J_{H,H}$ = 6.4 Hz, 1 H, =C*H*CH_3), 4.71 (m, 1 H, RhCH), 3.42, 3.23 (both m, 2 H, PC*H*CH_3), 2.15 (s, 3 H, CO_2CH_3), 1.53 (dd, $^3J_{H,H}$ = 6.8, $^5J_{H,H}$ = 2.7 Hz, 3 H, =CHC*H*$_3$), 1.15 (dd, $^3J_{H,H}$ = 16.1, $^3J_{P,H}$ = 7.0 Hz, 3 H, PCHC*H*$_3$), 1.03 (dd, $^3J_{H,H}$ = 14.3, $^3J_{P,H}$ = 7.0 Hz, 3 H, PCHC*H*$_3$), 1.02 (dd, $^3J_{H,H}$ = 16.0, $^3J_{P,H}$ = 6.8 Hz, 3 H, PCHC*H*$_3$), 0.89 (dd, $^3J_{H,H}$ = 15.1, $^3J_{P,H}$ = 6.8 Hz, 3 H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 198.1

(s, RhCH=*C*), 189.4 (s, O_2CCH_3), 134.6 (d, $^3J_{P,C}$ = 7.5 Hz, *meta*-C of Ph), 134.3 (d, $^3J_{P,C}$ = 6.6 Hz, *meta*-C of Ph), 133.9 (d, $^3J_{P,C}$ = 7.4 Hz, *meta*-C of Ph), 133.7 (d, $^3J_{P,C}$ = 6.3 Hz, *meta*-C of Ph), 129.3, 129.0, 128.8, 128.5 (all s, *para*-C of Ph), 126.1 (d, $^2J_{P,C}$ = 8.7 Hz, *ortho*-C of Ph), 125.9 (d, $^2J_{P,C}$ = 9.0 Hz, *ortho*-C of Ph), 125.5 (d, $^2J_{P,C}$ = 10.0 Hz, *ortho*-C of Ph), 125.4 (d, $^1J_{P,C}$ = 50.0 Hz, *ipso*-C of Ph), 125.4 (d, $^1J_{P,C}$ = 52.1 Hz, *ipso*-C of Ph), 125.3 (d, $^2J_{P,C}$ = 10.2 Hz, *ortho*-C of Ph), 124.5 (d, $^1J_{P,C}$ = 46.0 Hz, *ipso*-C of Ph), 124.4 (d, $^1J_{P,C}$ = 48.2 Hz, *ipso*-C of Ph), 87.4 (dt, $^1J_{Rh,C}$ = 17.7, $^2J_{P,C}$ = 10.7 Hz, RhCH), 83.0 (s, =*C*HCH$_3$), 25.9 (d, $^1J_{P,C}$ = 25.9 Hz, P*C*HCH$_3$), 25.7(s, O_2CCH_3), 25.4 (d, $^1J_{P,C}$ = 26.5 Hz, P*C*HCH$_3$), 17.9, 17.7, 16.9, 16.7 (all s, PCH*C*H$_3$), 13.3 (s, = CH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ(A) = 51.8, δ(B) = 51.3 (ABX spin system, $J_{A,B}$ = 32.0 Hz, $J_{A,X}$ = $J_{B,X}$ = 139.4 Hz). MS (70 eV, e-spray): *m*/*z* = 671 [M$^+$ − Cl]. $C_{36}H_{42}ClO_2P_2Rh$ (707.0): calcd. C 61.16, H 5.99, Rh 14.55; found C 61.14, H 6.19, Rh 14.21.

Preparation of [Rh(κ^2-O_2CCH_3)(C≡CPh){(*E*)-C(CO$_2$Me)=CHCO$_2$Me}(P*i*PrPh$_2$)$_2$] (28): A solution of **21** (106 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) was treated at −20 °C with phenylacetylene (16 μL, 0.14 mmol) and stirred for 5 min at −20 °C. After a few seconds a change of color from yellow to red occurred, followed by a subsequent change of color in the opposite direction. After warming the solution to room temperature, the solvent was evaporated in vacuo and the residue extracted with acetone (20 mL). The extract was dried in vacuo to give a pale-yellow solid which was washed twice with 1-mL portions of acetone (0 °C) and dried; yield 99 mg (82%); m.p. 140 °C (dec.). IR (KBr): ν(C≡C) = 2100, ν(C=O) = 1695, ν(OCO) = 1570 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 8.11−6.99 (m, 25 H, C_6H_5), 6.00 (s, 1 H, =C*H*CO$_2$CH$_3$), 3.80 (s, 3 H, CO$_2$CH$_3$), 3.52 (m, 2 H, PC*H*CH$_3$), 3.37 (s, 3 H, CO$_2$CH$_3$), 1.40 (dvt, *N* = 15.4, $^3J_{H,H}$ = 7.7 Hz, 6 H, PCHC*H*$_3$), 0.99 (dvt, *N* = 14.6, $^3J_{H,H}$ = 7.3 Hz, 6 H, PCHC*H*$_3$), 0.98 (s, 3 H, O_2CCH_3). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 34.3 (d, $^1J_{Rh,P}$ = 97.4 Hz). $C_{46}H_{49}O_6P_2Rh$ (862.7): calcd. C 64.04, H 5.72, Rh 11.93; found C 63.51, H 5.66, Rh 11.87.

Preparation of [Rh{κ^2-O$_2$CC(CH$_3$)$_3$}(C≡CPh){(*E*)-C(CO$_2$Me)=CHCO$_2$Me}(P*i*PrPh$_2$)$_2$] (29): This compound was prepared as described for **28**, with **22** (96 mg, 0.12 mmol) and phenylacetylene (14 μL, 0.12 mmol) as starting materials. Pale-yellow solid; yield 93 mg (86%); m.p. 116 °C (dec.). IR (KBr): ν(C≡C) = 2100, ν(C=O) = 1695, ν(OCO) = 1570 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.98−7.03 (m, 25 H, C_6H_5), 6.04 (s, 1 H, =C*H*CO$_2$CH$_3$), 3.89 (s, 3 H, CO$_2$CH$_3$), 3.54 (m, 2 H, PC*H*CH$_3$), 3.40 (s, 3 H, CO$_2$CH$_3$), 1.33 (dvt, *N* = 15.0, $^3J_{H,H}$ = 7.5 Hz, 6 H, PCHC*H*$_3$), 1.04 (dvt, *N* = 14.4, $^3J_{H,H}$ = 7.5 Hz, 6 H, PCHC*H*$_3$), 0.70 [s, 9 H, C(*C*H$_3$)$_3$]. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 192.1 [s, $O_2CC(CH_3)_3$], 173.1, 162.2 (both s, *C*O$_2$CH$_3$), 162.2 [dt, $^1J_{Rh,C}$ = 33.9, $^2J_{P,C}$ = 9.5 Hz, Rh*C*(CO$_2$CH$_3$)], 136.5−125.4 (m, C_6H_5), 120.5 (dt, $^2J_{Rh,C}$ = 4.3, $^3J_{P,C}$ = 4.3 Hz, =*C*HCO$_2$CH$_3$), 106.6 (dt, $^2J_{Rh,C}$ = 8.6, $^3J_{P,C}$ = 1.9 Hz, ≡*C*C$_6$H$_5$), 100.2 (dt, $^1J_{RhC}$ = 48.6, $^2J_{P,C}$ = 20.5 Hz, Rh*C*≡C), 51.0, 50.3 (both s, CO$_2$*C*H$_3$), 39.6 [s, *C*(CH$_3$)$_3$], 27.0 (vt, *N* = 25.3 Hz, P*C*HCH$_3$) 26.7 [s, C(*C*H$_3$)$_3$], 20.1, 19.1 (both s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 31.8 (d, $^1J_{Rh,P}$ = 97.2 Hz). $C_{49}H_{54}O_6P_2Rh$ (903.8): calcd. C 65.12, H 6.02; found C 65.44, H 6.18.

Preparation of [RhCl(C≡CPh){(*E*)-C(CO$_2$Me)=CHCO$_2$Me}(P*i*PrPh$_2$)$_2$] (30): A solution of either **28** (121 mg, 0.14 mmol) or **29** (127 mg, 0.14 mmol) in acetone (5 mL) was treated with freshly distilled Me$_3$SiCl (18 μL, 0.14 mmol) and stirred for 10 min at −20 °C. A rapid change of color from pale-yellow to red occurred. After warming the solution to room temperature and evaporating the solvent in vacuo, a red, thermally labile oil was obtained; yield 108 mg (92%) from **28** and 110 mg (94%) from **29**. IR (C_6H_6): ν(C≡C) = 2100, ν(C=O) = 1700 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 8.16−6.66 (m, 25 H, C_6H_5), 6.04 (s, 1 H, = C*H*CO$_2$CH$_3$), 3.98 (m, 2 H, PC*H*CH$_3$), 3.12, 2.99 (both s, 3 H each, CO$_2$CH$_3$), 1.44 (dvt, *N* = 15.2, $^3J_{H,H}$ = 7.8 Hz, 6 H, PCHC*H*$_3$), 1.15 (dvt, *N* = 14.6, $^3J_{H,H}$ = 7.2 Hz, 6 H, PCHC*H*$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ = 18.9 (d, $^1J_{Rh,P}$ = 94.3 Hz); $C_{44}ClH_{46}O_4P_2Rh$ (839.2): calcd. C 62.98, H 5.53; found C 63.04, H 6.00.

Preparation of *trans*-[RhCl{η^2-PhC≡CC(CO$_2$Me)=CHCO$_2$Me}(P*i*PrPh$_2$)$_2$] (31): A solution of **30** (109 mg, 0.13 mmol) was stirred for 1 h at 60 °C. A change of color from red to orange occurred. After cooling the solution to room temperature, the solvent was removed in vacuo, and the residue was extracted with acetone (20 mL). The extract was dried in vacuo to give an orange solid which was washed twice with 1-mL portions of acetone (0 °C) and dried; yield 82 mg (75%); m.p. 104 °C (dec.). IR (KBr): ν(C≡C) = 1835, ν(C=O) = 1704, ν(C=C) = 1565 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 8.19−6.91 (m, 25 H, C_6H_5), 6.70 (s, 1 H, = C*H*CO$_2$CH$_3$), 3.48, 3.32 (both s, 3 H each, CO$_2$CH$_3$), 3.10 (m, 2 H, PC*H*CH$_3$), 1.35 (dvt, *N* = 15.0, $^3J_{H,H}$ = 7.3 Hz, 6 H, PCHC*H*$_3$), 1.19 (dvt, *N* = 15.4, $^3J_{H,H}$ = 7.3 Hz, 6 H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 166.5, 165.7 (both s, CO$_2$), 130.9 (s, = *C*CO$_2$CH$_3$), 173.0−124.9 (m, C_6H_5), 120.2 (s, =*C*HCO$_2$CH$_3$), 108.5 (dt, $^1J_{RhC}$ = 15.3, $^2J_{P,C}$ = 2.9 Hz, Ph*C*≡C), 81.7 (dt, $^1J_{RhC}$ = 16.2, $^2J_{P,C}$ = 2.0 Hz, PhC≡*C*), 51.9, 51.5 (both s, CO$_2$*C*H$_3$), 25.4 (vt, *N* = 23.5 Hz, P*C*HCH$_3$), 19.9, 19.3 (both s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 36.6 (d, $^1J_{RhP}$ = 117.7 Hz). MS (70 eV, e-spray): *m*/*z* = 803 [M$^+$ − Cl]. $C_{44}H_{46}ClO_4P_2Rh$ (839.2): calcd. C 62.98, H 5.53; found C 63.03, H 6.01.

Reaction of 31 with CO: A slow stream of CO was passed through a solution of **31** (84 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) at room temperature for 10 s. An instantaneous change of color from orange to yellow occurred. The ^{1}H NMR spectrum of the solution indicated that the enyne **33** was formed along with **32**.[23] The solvent was evaporated in vacuo, the remaining yellow solid was washed twice with 1-mL portions of acetone (0 °C) and identified as **32**; yield 62 mg (98%).

Preparation of *trans*-[RhCl(CO)(P*i*PrPh$_2$)$_2$] (32): A slow stream of CO was passed through a suspension of **3** (48 mg, 0.04 mmol) in toluene (10 mL) at room temperature for 10 min. A change of color from violet to yellow occurred. After evaporation of the solvent in vacuo, the yellow solid was washed twice with 1-mL portions of acetone (0 °C) and dried; yield 50 mg (99%); m.p. 140 °C. IR (KBr): ν(CO) = 1960 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.79−6.96 (m, 20 H, C_6H_5), 3.48 (m, 2 H, PC*H*CH$_3$), 1.10 (dvt, *N* = 15.5, $^3J_{H,H}$ = 7.5 Hz, 12 H, PCHC*H*$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 41.0 (d, $^1J_{Rh,P}$ = 123.5 Hz). $C_{31}H_{34}ClOP_2Rh$ (622.9): calcd. C 59.77, H 5.50, Rh 16.52; found C 60.21, H 5.99, Rh 16.74.

Preparation of [Rh{κ^1-O$_2$S(O)-*p*-Tol}(=C=CHPh)(P*i*Pr$_2$Ph)$_2$] (34): A solution of **12** (106 mg, 0.16 mmol) in toluene (2 mL) was treated with phenylacetylene (19 μL, 0.16 mmol) and stirred for 3 h at room temperature. A change of color from red to violet occurred. The solvent was evaporated in vacuo and the residue extracted with ether (25 mL). After drying the extract in vacuo, the remaining violet solid was washed twice with 10-mL portions of pentane (0 °C) and dried; yield 120 mg (98%); m.p. 67 °C (dec.). IR (CH_2Cl_2): ν(C=C) = 1650 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.75−6.56 (m, 19 H, C_6H_5 and C_6H_4), 2.82 (m, 4 H, PC*H*CH$_3$), 1.93 (s, 3 H, $C_6H_4CH_3$), 1.40 (dvt, *N* = 16.4, $^3J_{H,H}$ = 6.9 Hz, 12 H, PCHC*H*$_3$), 1.09 (dt, $^3J_{Rh,H}$ = 1.5, $^4J_{P,H}$ = 3.5 Hz, 1 H, =C*H*Ph), 0.93 (dvt,

N = 13.9, $^3J_{H,H}$ = 9.1 Hz, 12 H, PCHCH_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 306.9 (dt, $^1J_{Rh,C}$ = 58.4, $^2J_{P,C}$ = 18.1 Hz, Rh=*C*=C), 143.7, 139.4, 134.9, 129.9, 128.6, 128.5, 127.9, 127.7, 126.8, 126.2, 125.3, 124.6 (all s, C_6H_5 and C_6H_4), 113.4 (dt, $^2J_{Rh,C}$ = 15.3, $^3J_{P,C}$ = 6.7 Hz, Rh=C=*C*), 30.4 (s, $C_6H_4CH_3$), 23.2 (vt, N = 22.3 Hz, P*C*HCH$_3$), 20.0, 18.5 (both s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 43.3 (d, $^1J_{Rh,P}$ = 143.9 Hz). $C_{39}H_{51}O_3RhS$ (764.8): calcd. C 61.25, H 6.72; found C 60.87, H 6.68.

Preparation of [Rh{κ^1-O$_2$S(O)-*p*-Tol}(=C=CHCMe$_2$OH)(P*i*Pr$_2$Ph)$_2$] (35): This compound was prepared as described for **34**, with **12** (106 mg, 0.16 mmol) and HC≡CCMe$_2$(OH) (16 μL, 0.16 mmol) as starting materials; reaction time 1 h. Violet solid; yield 113 mg (95%); m.p. 58 °C (dec.). IR (CH_2Cl_2): ν(C=C) = 1635 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.59−6.81 (m, 14 H, C_6H_5 and C_6H_4), 2.87 (s, 3 H, $C_6H_4CH_3$), 2.57 (m, 4 H, PC*H*CH$_3$), 1.43 (dvt, N = 16.5, $^3J_{H,H}$ = 7.3 Hz, 12 H, PCHCH_3), 1.23 [s, 6 H, C(CH_3)$_2$OH], 1.05 (dvt, N = 13.9, $^3J_{H,H}$ = 6.9 Hz, 12 H, PCHCH_3), 1.00 (dt, $^3J_{Rh,H}$ = 0.6, $^4J_{P,H}$ = 3.1 Hz, 1 H, =C*H*R), signal of O*H* proton not found. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 308.2 (dt, $^1J_{Rh,C}$ = 59.9, $^2J_{P,C}$ = 16.4 Hz, Rh=*C*=C), 143.9, 139.5, 135.2, 133.5, 130.1, 128.7, 128.1, 127.0 (all s, C_6H_5 and C_6H_4), 115.7 (dt, $^2J_{Rh,C}$ = 15.3, $^3J_{P,C}$ = 5.9 Hz, Rh=C=*C*), 43.0 [s, *C*(CH$_3$)$_2$OH], 31.8 (s, $C_6H_4CH_3$), 28.2 [s, C(*C*H$_3$)$_2$OH], 25.0 (vt, N = 25.9 Hz, P*C*HCH$_3$), 20.2, 18.7 (both s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 42.4 (d, $^1J_{Rh,P}$ = 143.9 Hz). $C_{36}H_{53}O_4P_2RhS$ (746.7): calcd. 57.90, H 7.15; found C 58.06, H 6.97.

Preparation of [Rh(C≡CPh)(=C=CHPh)(P*i*Pr$_2$Ph)$_2$] (36): a) A solution of **12** (100 mg, 0.15 mmol) in a 1:1 mixture of toluene and freshly distilled triethylamine (5 mL) was treated with phenylacetylene (34 μL, 0.30 mmol) and stirred for 5 min at −20 °C. A smooth change of color from red to dark green occurred. After warming the solution to room temperature, the solvent was evaporated in vacuo and the residue was extracted with 25 mL of ether (0° C). The extract was dried in vacuo, the remaining residue was dissolved in 5 mL of pentane (0° C) and the solution stored at this temperature. Turquoise crystals precipitated after 1 min, which were filtered, washed twice with 1-mL portions of pentane (0 °C) and dried; yield 35 mg (34%).

b) A solution of **34** (107 mg, 0.14 mmol) in a 1:1 mixture of toluene and freshly distilled triethylamine (5 mL) was treated at −50 °C with phenylacetylene (15 μL, 0.14 mmol). A quick change of color from violet to dark green occurred. After warming the solution to room temperature, it was worked up as described for a). Turquoise crystals were obtained; yield 54 mg (56%); m.p. 78 °C (dec.). IR (KBr): ν(C≡C) = 2060, ν(C=C) = 1635 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.78−6.78 (m, 20 H, C_6H_5), 2.87 (m, 4 H, PC*H*CH$_3$), 1.42 (dvt, N = 17.9, $^3J_{H,H}$ = 6.9 Hz, 12 H, PCHCH_3), 1.28 (dt, $^3J_{Rh,H}$ = 0.7, $^4J_{P,H}$ = 3.7 Hz, 1 H, =C*H*Ph), 1.06 (dvt, N = 13.9, $^3J_{H,H}$ = 6.9 Hz, 12 H, PCHCH_3). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 46.8 (d, $^1J_{Rh,P}$ = 141.0 Hz). $C_{40}H_{49}P_2Rh$ (694.7): calcd. C 69.16, H 7.11, Rh 14.81; found C 68.62, H 7.08, Rh 14.40.

Preparation of [Rh(C≡CCMe$_2$OH)(=C=CHCMe$_2$OH)(P*i*Pr$_2$Ph)$_2$] (37): This compound was prepared as described for **36**, either according to method a) from **12** (106 mg, 0.16 mmol) and HC≡CCMe$_2$(OH) (32 μL, 0.32 mmol) or according to method b) from **35** (106 mg, 0.14 mmol) and HC≡CCMe$_2$(OH) (14 μL, 0.14 mmol). Dark green solid; yield 47 mg (45%) for a) and 63 mg (68%) for b); m.p. 78 °C (dec.). IR (KBr): ν(OH) = 3555, 3540, ν(C≡C) = 2060, ν(C=C) = 1625 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.44−7.04 (m, 10 H, C_6H_5), 2.88 (m, 4 H, PC*H*CH$_3$), 1.62 (s, 1 H, OH), 1.45 [s, 6 H, C(CH_3)$_2$OH], 1.36 (dvt, N = 16.1, $^3J_{H,H}$ = 7.3 Hz, 12 H, PCHCH_3), 1.06 (dvt, N = 13.5, $^3J_{H,H}$ = 6.2 Hz, 12 H, PCHCH_3), 0.92 [s, 6 H, C(CH_3)$_2$OH], 0.21 (dt, $^3J_{Rh,H}$ = 0.7, $^4J_{P,H}$ = 3.7 Hz, 1 H, =CHR), signal of the second OH proton not found. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 45.7 (d, $^1J_{Rh,P}$ = 142.4 Hz). $C_{34}H_{53}O_2P_2Rh$ (658.7): calcd. C 62.00, H 8.11; found C 61.59, H 8.10.

Preparation of [Rh(C≡CCMe$_2$OH)(=C=CHPh)(P*i*Pr$_2$Ph)$_2$] (38): A solution of **34** (115 mg, 0.15 mmol) in a 1:1 mixture of toluene and freshly distilled triethylamine (5 mL) was treated at −50 °C with HC≡CCMe$_2$(OH) (15 μL, 0.15 mmol) and stirred for 5 min at this temperature. A change of color from violet to dark green occurred. After warming the solution to room temperature, the solvent was evaporated in vacuo. The residue was extracted with 25 mL of ether (0 °C) and the extract was dried in vacuo. The residue was dissolved in 3 mL of acetone (0 °C) and the solution stored for 3 min at this temperature. Dark green crystals precipitated, which were filtered, washed twice with 1-mL portions of acetone (0 °C) and dried; yield 40 mg (39%); m.p. 98 °C (dec.). IR (KBr): ν(OH) = 3350, ν(C≡C) = 2060, ν(C=C) = 1635 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.44−7.04 (m, 15 H, C_6H_5), 3.12 (m, 4 H, PC*H*CH$_3$), 1.60 (dvt, N = 15.7, $^3J_{H,H}$ = 8.0 Hz, 12 H, PCHCH_3), 1.20 (dvt, N = 13.3, $^3J_{H,H}$ = 6.6 Hz, 12 H, PCHCH_3), 1.07 [s, 6 H, C(CH_3)$_2$OH], 0.96 (dt, $^3J_{Rh,H}$ = 0.8, $^4J_{P,H}$ = 3.6 Hz, 1 H, =CHR), signal of OH proton not found. ^{31}P NMR (162.0 MHz, C_6D_6): δ = 45.9 (d, $^1J_{Rh,P}$ = 141.0 Hz). $C_{37}H_{51}OP_2Rh$ (676.7): calcd. C 65.68, H 7.60; found C 65.33, H 7.48.

Preparation of *trans*-[Rh{(*Z*)-C(=CHPh)C≡CPh}(CO)(P*i*Pr$_2$Ph)$_2$] (39): A slow stream of CO was passed through a solution of **36** (97 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) at −20 °C for 10 s. A change of color from dark green to yellow occurred. After warming the solution to room temperature, the solvent was evaporated in vacuo. The residue was extracted with 25 mL of acetone (10 °C) and the extract was dried in vacuo. The remaining yellow solid was washed twice with 1-mL portions of acetone (0 °C) and dried; yield 87 mg (86%); m.p. 144 °C (dec.). IR (KBr): ν(C≡C) = 2120, ν(CO) = 1955 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 8.07 (dt, $^3J_{Rh,H}$ = 2.2, $^4J_{P,H}$ = 9.5 Hz, 1 H, =C*H*Ph), 7.81−6.94 (m, 20 H, C_6H_5), 2.78, 2.41 (both m, 2 H each, PC*H*CH$_3$), 2.26 (dvt, N = 15.9, $^3J_{H,H}$ = 7.0 Hz, 6 H, PCHCH_3), 1.13 (dvt, N = 15.0, $^3J_{H,H}$ = 7.3 Hz, 6 H, PCHCH_3), 0.87 (dvt, N = 15.2, $^3J_{H,H}$ = 6.6 Hz, 6 H, PCHCH_3), 0.65 (dvt, N = 16.1, $^3J_{H,H}$ = 7.3 Hz, 6 H, PCHCH_3). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 41.4 (d, $^1J_{Rh,P}$ = 145.3 Hz). $C_{41}H_{49}OP_2Rh$ (722.7): calcd. C 68.14, H 6.83; found C 67.80, H 7.28.

Preparation of *trans*-[Rh{(*Z*)-C(=CHCMe$_2$OH)C≡CCMe$_2$OH}(CO)(P*i*Pr$_2$Ph)$_2$] (40): This compound was prepared as described for **39**, with **37** (86 mg, 0.13 mmol) and CO as starting materials. Yellow solid; yield 75 mg (84%); m.p. 80 °C (dec.). IR (KBr): ν(C≡C) = 2160, ν(CO) = 1955 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 8.20−7.34 (m, 10 H, C_6H_5), 7.18 (dt, $^3J_{Rh,H}$ = 2.6, $^4J_{P,H}$ = 2.2 Hz, 1 H, =C*H*R), 4.64 (s, 1 H, OH), 3.00, 2.73 (both m, 2 H each, PC*H*CH$_3$), 2.00 (s, 1 H, OH), 1.97 [s, 6 H, C(CH_3)$_2$OH], 1.70 (dvt, N = 16.5, $^3J_{H,H}$ = 9.5 Hz, 6 H, PCHCH_3), 1.46 [s, 6 H, C(CH_3)$_2$OH], 1.42 (dvt, N = 13.9, $^3J_{H,H}$ = 8.4 Hz, 6 H, PCHCH_3), 1.35 (dvt, N = 12.1, $^3J_{H,H}$ = 6.6 Hz, 6 H, PCHCH_3), 1.25 (dvt, N = 13.9, $^3J_{H,H}$ = 7.3 Hz, 6 H, PCHCH_3). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 39.1 (d, $^1J_{Rh,P}$ = 142.4 Hz). $C_{35}H_{53}O_3P_2Rh$ (686.7): calcd. C 61.22, H 7.78; found C 61.53, H 7.72.

Preparation of *trans*-[Rh{(*Z*)-C(=CHPh)C≡CCMe$_2$OH}(CO)(P*i*Pr$_2$Ph)$_2$] (41): This compound was prepared as described for **39**,

with **38** (101 mg, 0.15 mmol) and CO as starting materials. Yellow oil; yield 40 mg (38%). IR (KBr): ν(C≡C) = 2070, ν(CO) 1950 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.93−7.25 (m, 15 H, C_6H_5), 7.20 (dt, $^3J_{Rh,H}$ = 2.4, $^4J_{P,H}$ = 2.2 Hz, 1 H, =C*H*R), 4.53 (s, 1 H, OH), 2.77, 2.51 (both m, 2 H each, PC*H*CH$_3$), 1.46 (dvt, *N* = 16.5, $^3J_{H,H}$ = 6.9 Hz, 6 H, PCHC*H*$_3$), 1.25 (dvt, *N* = 15.7, $^3J_{H,H}$ = 6.9 Hz, 6 H, PCHC*H*$_3$), 1.23 [s, 6 H, C(C*H*$_3$)$_2$OH], 1.12 (dvt, *N* = 13.5, $^3J_{H,H}$ = 6.9 Hz, 6 H, PCHC*H*$_3$), 1.00 (dvt, *N* = 14.3, $^3J_{H,H}$ = 6.6 Hz, 6 H, PCHC*H*$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ = 39.1 (d, $^1J_{Rh,P}$ = 140.9 Hz). $C_{38}H_{51}O_2P_2Rh$ (704.7): calcd. C 64.77 H 7.29, Rh 14.60; found C 64.68 H 7.34, Rh 14.22.

Determination of the X-ray Crystal Structure of 27: Single crystals were grown upon diffusion of ether into a saturated solution of **27** in CH_2Cl_2/methylcyclohexane. Crystal data (from 23 reflections, 10° < Θ < 14°): monoclinic; space group $P2_1/c$ (No. 14); *a* = 10.496(5), *b* = 17.455(5), *c* = 18.629(7) Å, β = 97.33(2)°; *V* = 3385(2) Å^3, *Z* = 4; $d_{calcd.}$ = 1.387 g cm^{-3}; μ(Mo-K_α) = 7.0 cm^{-1}; crystal size 0.23 × 0.38 × 0.48 mm; Enraf−Nonius CAD4, Mo-K_α radiation (0.71073 Å), graphite monochromator; *T* = 293(2) K; Θ-scan, max. 2Θ = 47.94°; 5011 reflections measured, 4691 independent, 3135 with $I > 2\sigma(I)$. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied. The structure was solved by direct method (SHELXS-86).[28] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares method using the program package SDP from Enraf−Nonius. The hydrogen atoms H1 and H3 were found in a difference-Fourier synthesis and refined isotropically. The positions of all other hydrogen atoms were calculated according to ideal geometry and refined with the riding method. Conventional R = 0.0421 and weighted wR_2 = 0.0857 [for data with $I > 2\sigma(I)$]; R = 0.1019 and weighted wR_2 = 0.0991 (for all data); reflection/parameter ratio 12.1; residual electron density +0.939/−0.323 eÅ^{-3}.

CCDC-175652 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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