An Unprecedented Type of Migratory Insertion Reactions of Unsaturated C_3 Units into Rh–O and Rh–C Bonds

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Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 60th birthday

Abstract: A series of iodo- and hydroxorhodium(I) complexes of the general composition *trans*-[RhX(=C=C=CRR′)(P*i*Pr$_3$)$_2$] (X = I: **5**–**7**; X = OH: **8**–**11**) was prepared from the related chlororhodium(I) precursors. The hydroxo compounds behave as organometallic Brønsted bases and react with acids like MeCO$_2$H, PhCO$_2$H, PhOH, or TsOH by elimination of water to give the substitution products *trans*-[RhX′(=C=C=CRR′)(P*i*Pr$_3$)$_2$] (X′ = MeCO$_2$: **12**, **13**; X′ = PhCO$_2$: **14**; X′ = PhO: **15**, **16**; X′ = TsO: **17**, **18**) in good to excellent yields. In contrast to the tosylates **17**, **18**, which react with CO by cleavage of the allenylidene–metal bond to give *trans*-[Rh(OTs)(CO)(P*i*Pr$_3$)$_2$] (**19**), treatment of the acetato and phenolato derivatives **12**, **13** and **15**, **16** with CO affords by migratory insertion of the allenylidene unit into the Rh–O bond the alkynyl complexes *trans*-[Rh{C≡CCR(R′)X′}(CO)(P*i*Pr$_3$)$_2$] (X′ = MeCO$_2$: **20**, **21**; X′ = OPh: **22**, **23**). Similarly, the reactions of the hydroxo compounds **8**, **10**, and **11** with CH$_2$(CN)$_2$ and either CO or CNMe yield the carbonyl and the isocyanide complexes *trans*-[Rh{C≡CCR(R′)CH(CN)$_2$}(L′)(P*i*Pr$_3$)$_2$] (L′ = CO: **25**–**27**; L′ = CNMe: **28**–**30**), respectively. By protolytic cleavage of the Rh–C σ bond the γ-functionalized alkynes HC≡CCR(R′)CH(CN)$_2$ (**31**, **32**) are generated from **25**, **26** and HCl in benzene. The molecular structure of **22** was determined by X-ray crystallography.

Keywords: alkynes · allenylidene complexes · hydroxo complexes · insertion · rhodium

Introduction

In the context of our studies on the chemistry of square-planar rhodium(I) complexes containing vinylidenes as ligands, we recently observed that the reaction of *trans*-[Rh(R′)(=C=CHR)(P*i*Pr$_3$)$_2$] (where R′ is an alkyl, aryl, vinyl, or alkynyl ligand) with CO leads to the formation of substituted η^1-vinylrhodium(I) compounds *trans*-[Rh{η^1-(*Z*)-C(R′)=CHR}(CO)(P*i*Pr$_3$)$_2$] by C–C coupling of the R′ and C=CHR units.[1] Even in the absence of CO, the corresponding methyl and vinyl derivatives, *trans*-[Rh(CH$_3$)(=C=CHR)(P*i*Pr$_3$)$_2$] and *trans*-[Rh(CH=CH$_2$)(=C=CHR)(P*i*Pr$_3$)$_2$] rearrange to give the isomeric η^3-allyl- and η^3-butadienylrhodium(I) complexes, respectively.[1b, 2]

This unprecedented type of migratory insertion reaction prompted us to prepare also the related allenylidene compounds *trans*-[Rh(R′)(=C=C=CR$_2$)(P*i*Pr$_3$)$_2$] from *trans*-[RhCl(=C=C=CR$_2$)(P*i*Pr$_3$)$_2$] and either Grignard reagents or organolithium compounds as the precursors. Quite unexpectedly, all these attempts failed. We found, however, that the chloro derivatives react with sodium azide to give by salt metathesis the azido complexes *trans*-[Rh(N$_3$)(=C=C=CR$_2$)(P*i*Pr$_3$)$_2$], which in the presence of CO undergo an insertion of the allenylidene ligand into the Rh–N$_3$ bond.[3] For R = aryl, the insertion product (bearing the N$_3$ substituent at the γ-carbon atom) is rather labile and rearranges to the metalated acrylonitrile compounds *trans*-[Rh{C(CN)=CR$_2$)}(CO)(P*i*Pr$_3$)$_2$] by elimination of N$_2$.

The results presented herein illustrate that an unsaturated C_3 unit cannot only be inserted into a Rh–N but also into a Rh–O or a Rh–C bond. In this case, the precondition was the synthesis of the hydroxorhodium(I) complexes *trans*-[Rh(OH)(=C=C=CRR′)(P*i*Pr$_3$)$_2$] which behave as organometallic Brønsted bases and react with Brønsted acids to afford the starting materials that undergo migratory insertion reactions. A few results of this work have already been communicated.[4]

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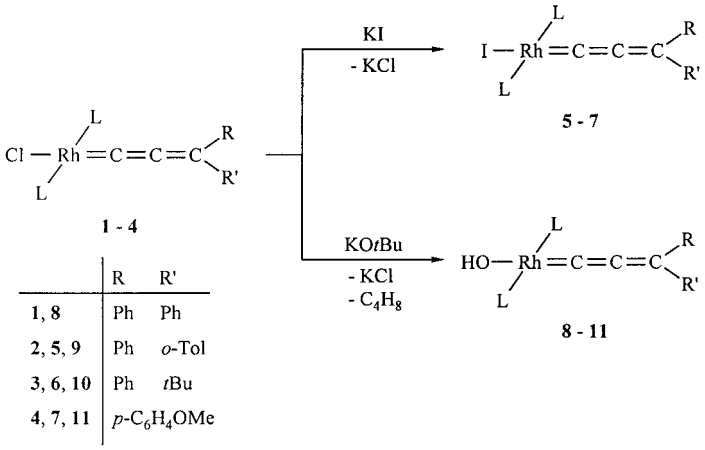
Results and Discussion

Square-planar allenylidenerhodium(I) complexes with anionic O-donor ligands: Taking the increasing lability of the Rh–X bond in the order Cl < Br < I into account, we considered the

iodo compounds *trans*-[RhI(=C=C=CRR′)(P*i*Pr$_3$)$_2$] as useful precursors for the preparation of related rhodium(I) complexes with carboxylates, tosylate (OTs), or phenolate as ligands. The synthesis of the iodo compounds **5**–**7** (Scheme 1)



	R	R′
1, 8	Ph	Ph
2, 5, 9	Ph	*o*-Tol
3, 6, 10	Ph	*t*Bu
4, 7, 11	*p*-C_6H_4OMe	

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

was straightforward and occurred by salt metathesis of the chloro derivatives with KI in THF. The dark red, only moderately air-sensitive solids, the spectroscopic data of which are quite similar to those of **2**–**4**, were isolated in virtually quantitative yield.

However, in contrast to what we expected, the iodo compounds proved to be rather inert and did not react with CH_3CO_2Na or NaOTs by ligand substitution. The more appropriate starting materials are the hydroxo complexes **8**–**11** which can be prepared on two different routes. The most convenient one consists of the reaction of the chloro derivatives **1**–**4** with KO*t*Bu in a mixture of benzene and *tert*-butyl alcohol (ratio 10:1) as the solvent. Alternatively, the organometallic hydroxides **8**–**11** can be obtained by treatment of the precursors **1**–**4** in benzene with 40% aqueous NaOH in the presence of [$PhCH_2NEt_3$]Cl (TEBA) as phase-transfer reagent. This preparative procedure is somewhat similar to that for the syntheses of the dimers [Rh(μ-OH)(PR$_3$)$_2$]$_2$ (R = Ph,[5] *i*Pr[6]) and of the vinylidene analogue *trans*-[Rh(OH)(=C=CHPh)(P*i*Pr$_3$)$_2$],[7] which also proceed in benzene/water under biphasic conditions. With regard to the more efficient route (reaction of **1**–**4** with KO*t*Bu) we note that Bergman and Woerpel recently observed that the hydroxoiridium(III) complex [(η^5-C_5Me_5)Ir(OH)(Ph)(PMe$_3$)] is accessible from the corresponding triflate [(η^5-C_5Me_5)-Ir(OTf)(Ph)(PMe$_3$)] and KO*t*Bu.[8] In either case (with rhodium(I) or iridium(III) as the metal center) it is reasonable to assume that an M(O*t*Bu) species is generated as an intermediate which looses isobutene to give the final product.

The new hydroxo compounds **8**–**11** are deeply colored, air- and moisture-sensitive solids which are soluble in most organic solvents including pentane. While the chloro complexes **1**–**4** are stable in benzene for days, the hydroxo derivatives slowly decompose in C_6H_6 in 12–24 h to give some unidentified products. Characteristic spectroscopic features of **8**–**11** are the OH stretching mode at 3620–3650 cm^{-1} in the IR spectra, the single resonance (doublet) at δ = 40–42 in the ^{31}P NMR spectra confirming the *trans.* disposition of the phosphane ligands, and the two low-field resonances (both doublets of triplets) at around δ = 220–250 in the ^{13}C NMR spectra assigned to the α- and β-carbon atoms of the Rh=C=C=C chain.

The results of the reactivity studies of the hydroxo complexes **8** and **9** toward OH-acidic substrates are summarized in Scheme 2. The corresponding acid–base reactions proceed in benzene or THF at room temperature and afford the substitution products **12**–**18** in good to excellent yield. Only for the preparation of the tosylates **17** and **18** it is necessary to add the solution of the acid at −20 °C in order to avoid decomposition. Similarly to the Rh-OH precursors, compounds **12**–**18** are thermally quite stable and for short period of times can be handled on air. The IR spectra of the acetato derivatives **12** and **13** display a relatively strong band at 1705 (**12**) or 1710 cm^{-1} (**13**), which is assigned to the asymmetric OCO stretching mode, and in agreement with published data[9] supports the monodentate coordination of the OAc ligand. Related vinylidenerhodium(I) compounds *trans*-[Rh(OAc)(=C=CHR)(P*i*Pr$_3$)$_2$] are also known but have been prepared from the chelate complex [Rh(κ^2-O_2CMe)-(P*i*Pr$_3$)$_2$] and terminal alkynes.[10] Attempts to obtain the allenylidene counterpart **12** on a similar route from [Rh(κ^2-O_2CMe)(P*i*Pr$_3$)$_2$] and HC≡CCPh_2OH remained unsuccessful.

The preparation of the phenolato complexes **15** and **16** deserves a particular comment. Since it is known[11] that rhodium(I) and iridium(I) compounds *trans*-[M(OR′)-(CO)(PR$_3$)$_2$] having an alkoxy or aroxy ligand OR′ can be obtained either by salt metathesis from *trans*-

Abstract in German: *Eine Reihe von Iodo- und Hydroxo-rhodium(I)-Komplexen der allgemeinen Zusammensetzung trans-[RhX(=C=C=CRR′)(PiPr$_3$)$_2$] (X = I: **5**–**7**; X = OH: **8**–**11**) wurde aus den entsprechenden Chlororhodium(I)-Vorläufern hergestellt. Die Hydroxo-Verbindungen verhalten sich wie metallorganische Broensted-Basen und reagieren mit Säuren wie z. B. $MeCO_2H$; $PhCO_2H$; PhOH oder TsOH unter Abspaltung von Wasser mit guter bis sehr guter Ausbeute zu den Substitutionsprodukten trans-[RhX′(=C=C=CRR′)-(PiPr$_3$)$_2$] (X′ = $MeCO_2$: **12**, **13**; X′ = $PhCO_2$: **14**; X′ = PhO: **15**, **16**; X′ = TsO: **17**, **18**). Im Gegensatz zu den Tosylaten **17**, **18**, die mit CO unter Spaltung der Allenyliden-Metall-Bindung zu trans-[Rh(OTs)(CO)(PiPr$_3$)$_2$] (**19**) reagieren, führt die Einwirkung von CO auf die Acetato- und Phenolato-Derivate **12**, **13** und **15**, **16** unter Einschiebung der Allenyliden-Einheit in die Rh-O-Bindung zu den Alkinylkomplexen trans-[Rh{C≡CCR(R′)X′}(CO)(PiPr$_3$)$_2$] (X′ = $MeCO_2$: **20**, **21**; X′ = OPh: **22**, **23**). In analoger Weise liefern die Reaktionen der Hydroxo-Verbindungen **8**, **10** und **11** mit $CH_2(CN)_2$ und CO oder CNMe die Carbonyl- bzw. Isocyanid-Komplexe [Rh{C≡CCR(R′)CH(CN)$_2$}(L′)(PiPr$_3$)$_2$] (L′ = CO: **25**–**27**; L′ = CNMe: **28**–**30**). Durch protolytische Spaltung der Rh-C-σ-Bindung werden aus **25**, **26** und HCl in Benzol die γ-funktionalisierten Alkine HC≡CCR(R′)CH(CN)$_2$ (**31**, **32**) erhalten. Die Molekülstruktur von **22** wurde kristallographisch bestimmt.*

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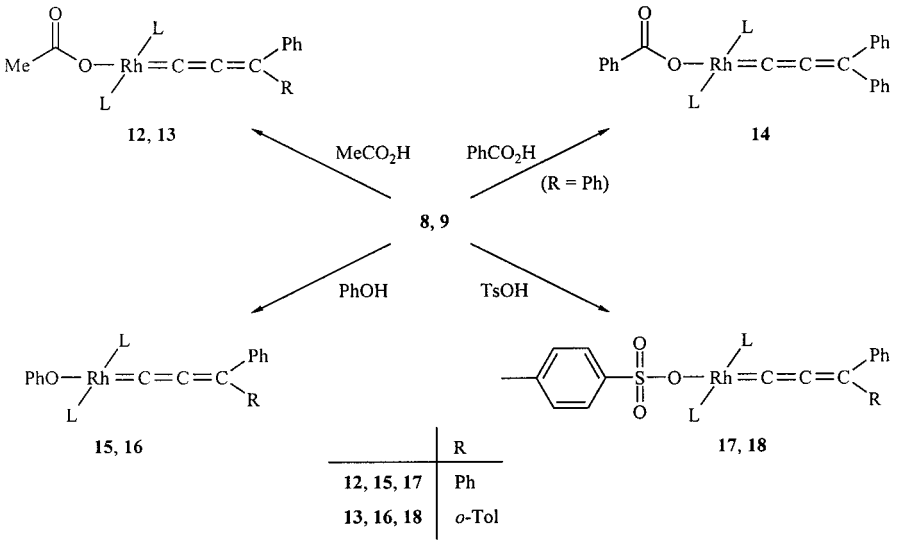
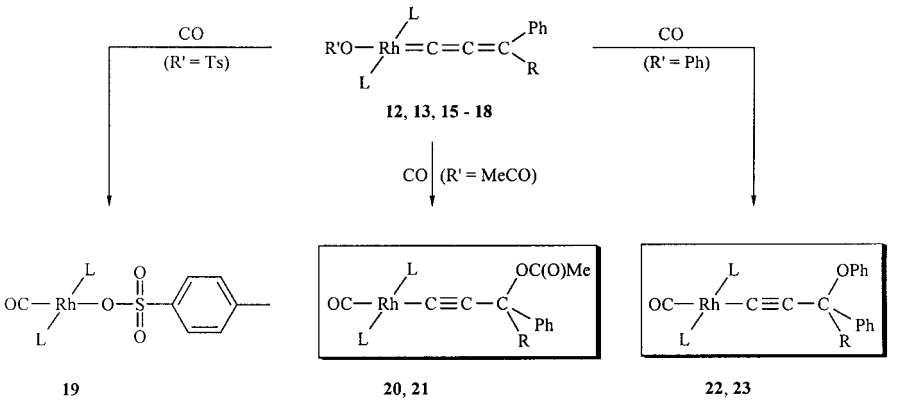


Scheme 2. L = P*i*Pr$_3$.

[MCl(CO)(PR$_3$)$_2$] and NaOR′ or from related cationic precursors, we equally attempted to prepare compound **15** from **1** or from *trans*-[Rh(acetone)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$]PF$_6$ and NaOPh. However, these attempts failed. Under the conditions used for the synthesis of **15** from **8** (see Scheme 2), there is also no attack of phenol at the allenylidene unit and thus rhodium(I) compounds such as **22** with a functionalized alkynyl ligand are not accessible from the corresponding hydroxo complex as the starting material.

Insertion reactions of the allenylidene unit into Rh–O bonds: Similarly to the azido complexes *trans*-[Rh(N$_3$)(=C=C=CR$_2$)(P*i*Pr$_3$)$_2$], the tosylato, acetato, and phenolato derivatives are also highly reactive toward carbon monoxide. Passing a slow stream of CO through a solution of **12**, **13** or **15**–**18** in benzene at room temperature for 30 s leads to a stepwise change of color from orange (or brown) to green and light yellow and, after removal of the solvent and recrystallization of the residue from acetone, to the formation of compounds **19**–**23** (Scheme 3) in 80–90% yield. However, while the analytical composition of **20**–**23** corresponds to that of a 1:1 adduct between the starting material and CO, the data for **19** indicate that in the course of the reactions of **12** and **13** with carbon monoxide the allenylidene ligand has been eliminated.



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

The product of the reactions of **12** and **13** with CO is the tosylato complex **19** (isolated as an orange, practically air-stable solid) of which the analogue *trans*-[Rh(OTs)(CO)(P*i*Pr$_2$Ph)$_2$] already exists.[12]

The structure of the carbonyl compounds **20**–**23**, generated from the acetato and phenolato complexes **15**–**18** and CO, is more noteworthy indeed. The ^{13}C NMR spectra display two signals (doublets of triplets) at around $\delta = 125-127$ and 114–115 which by comparison with other alkynylrhodium(I) compounds can be assigned to the carbon atoms of a C–C triple bond.[10, 13] Since in agreement with this, the IR spectrum of **20** exhibits a strong absorption at 2100 cm^{-1} corresponding to a C≡C stretching frequency, it is reasonable to assume that treatment of **15**–**18** with CO results in a migration of the anionic ligand to the allenylidene unit and that the acetate or phenolate group in the product is linked to the γ-carbon atom of the C$_3$ chain.

To substantiate the proposed stereochemistry, an X-ray crystal structure analysis of **22** was carried out. The ORTEP drawing (Figure 1) reveals that the rhodium is coordinated in a slightly distorted square-planar fashion with the two phosphane ligands in *trans* disposition. As expected, the Rh–C1 distance (2.037(4) Å) is significantly longer than in the allenylidene complex **2** (1.855(5) Å)[14] and nearly identical to the Rh–C bond lengths in the bis(alkynyl)rhodium(III) compound [RhH(C≡CC*i*Pr$_2$OH)$_2$(P*i*Pr$_3$)$_2$] (2.032(4) and 2.022(4) Å).[13d] The Rh-C-C-C chain is almost linear with only a slight bending at C1 and C2. The two phenyl groups at C3 are orthogonal to each other, thus presumably minimizing the repulsion between the C–H units of the rings. The distance Rh–C22 (1.830(4) Å) is very similar to the Rh–CO bond lengths in related carbonylrhodium(I) compounds.[15]

The observation that treatment of **15** with CO *in the presence of excess acetate ions* leads exclusively to the formation of **22** and that (by using ^{31}P NMR spectroscopy) even no traces of **20** could be detected, suggests that the migration of the coordinated phenolate to the allenylidene unit occurs *intra*molecularly. Since it is known that four-coordinate d^8 transition metal complexes react with Lewis bases preferentially by an S$_N$2-type mechanism,[16] we assume that in the initial step of the conversion of **15** to **22** a five-coordinate intermediate [Rh(OPh)(CO)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] with an 18-electron configuration at the

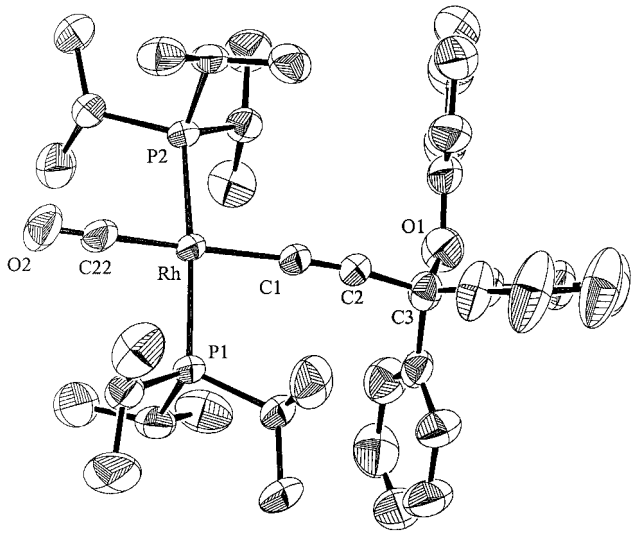
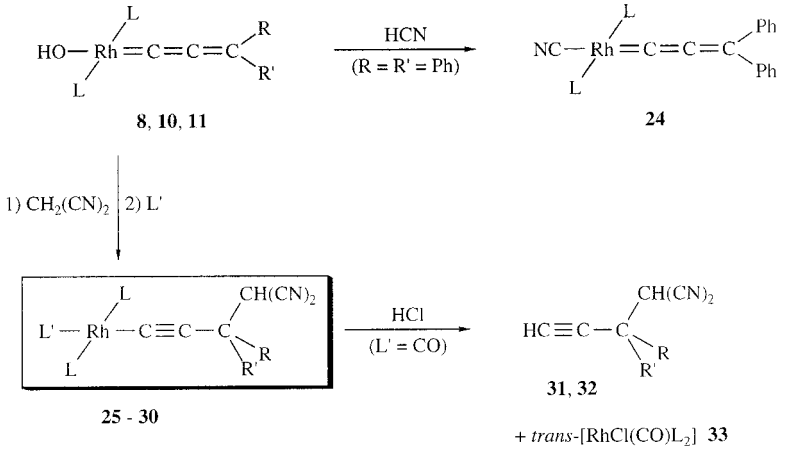


Figure 1. Molecular structure of **22**. Principal bond lengths [Å] and angles [°], with estimated standard deviations in parentheses: Rh–C1 2.037(4), Rh–P1 2.333(1), Rh–P2 2.331(1), Rh–C22 1.830(4), C1–C2 1.205(5), C2–C3 1.478(5), C3–O1 1.442(5), C22–O2 1.147(5); C1-Rh-C22 175.8(2), P1-Rh-P2 168.80(4), C1-Rh-P1 89.4(1), C1-Rh-P2 90.8(1), P1-Rh-C22 90.3(1), P2-Rh-C22 90.3(1), Rh-C1-C2 175.8(4), C1-C2-C3 173.0(4), C2-C3-O1 111.6(3), Rh-C22-O2 178.1(5).

metal center is formed. This species could rearrange to the more stable isomer **22**, the driving force probably being the preferred square-planar configuration of rhodium(I) compounds. By taking into consideration that the Rh–OPh bond is partially covalent in nature,[17] it seems less likely that in the migratory process leading to **22** (in benzene as solvent) an ionic intermediate $[Rh(CO)(=C=C=CPh_2)(P\mathit{i}Pr_3)_2]^+OPh^-$ is involved. In this context it is interesting to note that in contrast to the reaction of $[Pt(triphos)(OPh)]^+$ with CO which affords exclusively $[Pt(triphos)(CO_2Ph)]^+$ (triphos = bis[2-(diphenylphosphanyl)ethyl]phenylphosphane),[18] no insertion into the Rh–OPh bond takes place upon treatment of **15** with carbon monoxide.

Reactions of the hydroxorhodium(I) complexes with C-acids: Following the observation that compounds of the general composition *trans*-$[RhX(=C=C=CRR')(P\mathit{i}Pr_3)_2]$ with N- or O-bonded anionic ligands X react with CO by migratory insertion of the allenylidene unit into the Rh–X bond, we became interested to find out whether related complexes containing a C-bonded ligand X would behave similarly. After attempts to prepare alkyl or aryl derivatives (e.g. where X would be CH_3, *tert*-C_4H_9, C_6H_5) from *trans*-$[RhCl(=C=C=CRR')(P\mathit{i}Pr_3)_2]$ failed, we moved to the hydroxo compounds as the starting materials. While there was no reaction of **8** with PhC≡CH to give *trans*-$[Rh(C{\equiv}CPh)(=C=C=CPh_2)(P\mathit{i}Pr_3)_2]$, passing a stream of freshly generated HCN through a solution of **8** in benzene leads to the formation of the cyanorhodium(I) complex **24** (Scheme 4). The red, slightly air-sensitive solid is thermally quite stable (decomposition at 152 °C) and shows in the IR spectrum a strong absorption at 2100 cm^{-1} for the C≡N stretching mode. As already mentioned for the acetato derivatives **12** and **13**, the cyano compound **24** could also not be obtained by salt metathesis from **1** and NaCN.

Malodinitrile $CH_2(CN)_2$, having a similar pK_a (11.0) as phenol (10.0),[19] is also highly reactive toward **8**, **10**, and **11**. Addition of equimolar amounts of $CH_2(CN)_2$ to solutions of the organometallic hydroxides in benzene causes a rapid change of color from green (**8**, **10**) or red (**11**) to blue or violet, and gives, after evaporation of the solvent, oily residues, the NMR spectra of which (in C_6D_6) suggests that the anticipated compounds *trans*-$[Rh\{CH(CN)_2\}(=C=C=CRR')(P\mathit{i}Pr_3)_2]$ are formed. Due to the lability of the products (and the failure to crystallize the oily materials), we repeated the reactions of the starting materials **8**, **10**, and **11** with $CH_2(CN)_2$ in the presence of CO and obtained the alkynylrhodium(I) compounds **25**–**27** in 82–90 % yield. Methyl isocyanide behaves similarly to CO and transforms the postulated intermediates *trans*-$[Rh\{CH(CN)_2\}(=C=C=CRR')(P\mathit{i}Pr_3)_2]$ into the corresponding Rh(CNMe) derivatives **28**–**30** again with excellent yields. Both the carbonyl and the isocyanide complexes are yellow solids which are easily soluble (with the exception of pentane) in common organic solvents. The IR spectra of **25**–**30** display two strong absorptions at 2075–2095 (ν(C≡C)) and 1935–



	R	R'	L'
25	Ph	Ph	CO
26	Ph	*t*Bu	CO
27	*p*-C_6H_4OMe		CO
28	Ph	Ph	CNMe
29	Ph	*t*Bu	CNMe
30	*p*-C_6H_4OMe		CNMe

	R	R'
31	Ph	Ph
32	Ph	*t*Bu

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

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1945 cm^{-1} (ν(CO)) or 2055 cm^{-1} (ν(CNMe)), while the corresponding absorptions of the CN substituents at 2245–2255 cm^{-1} are of lower intensity. Characteristic features of the ^{13}C NMR spectra of **25**–**30** are the low-field resonance at $\delta \approx 195$ for the CO and at $\delta \approx 163$ for the *C*NMe carbon atom and the two signals at around at $\delta = 110-130$ for the carbon nuclei of the alkynyl unit. Since the γ-C atom of the RhC_3 chain of **26** is a center of chirality, the two CN groups of the $CH(CN)_2$ functionality are diastereotopic and therefore two singlets at $\delta = 114.0$ and 113.8 for the corresponding ^{13}C nuclei are observed. The ^1H NMR spectrum of **26** equally shows, in contrast to that of **25** and **27**, two resonances for the $PCHCH_3$ protons thus confirming the proposed stereochemistry.

Upon treatment of a solution of **25** and **26** in CH_2Cl_2 with a solution of HCl in benzene the bond between rhodium and the functionalized alkynyl ligand is split and the corresponding alkynes HC≡CCR(R′)$CH(CN)_2$ (**31**, **32**) are generated (see Scheme 4). The by-product is the chlororhodium(I) compound **33**.[20] The IR spectra of **31** and **32** show a typical band at about 3300 cm^{-1} for the alkyne C–H stretching mode, while the ^{13}C NMR spectra display two narrow signals at $\delta \approx 82$ and 79 for the alkyne carbon atoms. Although the available quantities of **31** and **32** were quite small, some preliminary experiments indicate that these novel functionalized alkynes react with $[RhCl(PiPr_3)_2]_2$ to give π-alkyne and subsequently the isomeric vinylidenerhodium(I) complexes.

Conclusion

Together with recent investigations from other laboratories,[21, 22] the work presented herein illustrates that metal allenylidenes offer a multifaceted chemistry indeed. As far as rhodium and *trans*-$Rh(PiPr_3)_2$ as a molecular building block are concerned, the important message is that besides *trans*-[RhX(=C=C=CRR′)$(PiPr_3)_2$] with X = Cl or F also the related hydroxo complexes **8**–**11** can be used as starting materials to incorporate anionic O-donor and C-donor ligands into the coordination sphere. The acetato (**12**, **13**), phenolato (**15**, **16**) and in situ generated substituted alkyl compounds *trans*-[Rh{$CH(CN)_2$}(=C=C=CRR′)$(PiPr_3)_2$] react with CO by migratory insertion of the allenylidene moiety into the Rh–O and Rh–C bond thus forming functionalized alkynyl ligands. Acid-induced cleavage of the Rh–C σ bond of the carbonyl complexes **25** and **26** affords the respective alkyne HC≡CCPh(R′)$CH(CN)_2$ (R′ = Ph, *t*Bu). This synthetic route supplements the recently reported preparation of vinylrhodium(I) complexes *trans*-[Rh{C(CN)=CRR′}$(CO)(PiPr_3)_2$] which upon treatment with acids generate acrylonitrile derivatives.[3]

Experimental Section

General considerations: All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by known procedures and distilled before use. The starting materials **1**–**4** were prepared as described in the literature.[3b, 14, 23]

Physical measurements: NMR spectra were recorded at room temperature or at the temperature mentioned in the appropriate procedure on Bruker AC 200 and Bruker AMX 400 instruments. Chemical shifts are expressed in ppm downfield from $SiMe_4$ (^1H and ^{13}C) and (85%) H_3PO_4 (^{31}P). Abbreviations used: s, singlet; d, doublet; t, triplet; vt, virtual triplet; $N = {}^3J(P,H)+{}^5J(P,H)$ or ${}^1J(P,C)+{}^3J(P,C)$; m, multiplet; br, broadened signal. Coupling constants *N* and *J* are given in Hertz. Mass spectra were measured on a Finnigan MAT instrument. Melting and decomposition points were determined by DTA.

Preparation of *trans*-[RhI{=C=C=C(*o*-Tol)Ph}$(PiPr_3)_2$] (5): A solution of **2** (110 mg, 0.17 mmol) in THF (5 mL) was treated with an excess of KI (166 mg, 1.00 mmol) and stirred for 3 h at room temperature. The solvent was removed in vacuo, and the residue was extracted with diethyl ether (10 mL). The extract was evaporated to dryness in vacuo, the residue was washed with pentane (2 × 1 mL; 0 °C) and then recrystallized from acetone (3 mL) at −78 °C. Red crystals were obtained which were separated from the mother liquor, washed with pentane (−20 °C), and dried; yield 116 mg (93%); m.p. 155 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 1870$ (ν(C=C=C)) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.76$ (br m, 9H; C_6H_4 and C_6H_5), 3.18 (m, 6H; $PCHCH_3$), 2.22 (s, 3H; $C_6H_4CH_3$), 1.47 (dvt, $N = 13.5$, $J(H,H) = 6.9$ Hz, 36H; $PCHCH_3$); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 244.7$ (dt, $J(Rh,C) = 16.0$, $J(P,C) = 8.0$ Hz; Rh=C=C=C), 218.7 (dt, $J(Rh,C) = 70.8$, $J(P,C) = 18.3$ Hz; Rh=C=C=C), 155.1, 154.2 (both s; *ipso*-C_6H_5 and *ipso*-C_6H_4Me), 146.8 (br s; Rh=C=C=*C*), 132.5, 130.9, 128.1, 127.6, 124.9, 124.8, 124.0, 118.5, (all s; C_6H_5 and C_6H_4), 25.0 (vt, $N = 31.4$ Hz; $PCHCH_3$), 20.9 (s; $PCHCH_3$), 20.3 (s; $C_6H_4CH_3$); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 34.6$ (d, $J(Rh,P) = 127.9$ Hz); elemental analysis (%) for $C_{34}H_{54}IP_2Rh$ (754.6): calcd: C 54.12, H 7.21; found: C 54.46, H, 7.48.

Preparation of *trans*-[RhI{=C=C=C(*t*Bu)Ph}$(PiPr_3)_2$] (6): This compound was prepared as described for **5**, from **3** (88 mg. 0.14 mmol) and excess KI (500 mg, 3.01 mmol) as starting materials. Dark red crystalline solid; yield 108 mg (97%); m.p. 128 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 1870$ (ν(C=C=C)) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.26$ (m, 2H; *o*-C_6H_5), 7.08 (m, 3H; *m*- and *p*-C_6H_5), 2.82 (m, 6H; $PCHCH_3$), 1.19 (dvt, $N = 13.4$, $J(H,H) = 7.1$ Hz, 36H; $PCHCH_3$), 1.08 (s, 9H; $C(CH_3)_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 239.9$ (dt, $J(Rh,C) = 70.4$, $J(P,C) = 17.1$ Hz; Rh=C=C=C), 231.6 (dt, $J(Rh,C) = 17.1$, $J(P,C) = 6.3$ Hz; Rh=C=C=C), 163.7 (br s; *ipso*-C_6H_5), 155.6 (br s; Rh=C=C=*C*), 126.8, 126.6, 117.8 (all s; C_6H_5), 52.8 (s; $C(CH_3)_3$), 25.3 (vt, $N = 20.0$ Hz; $PCHCH_3$), 24.2 (s; $C(CH_3)_3$), 20.20 (s; $PCHCH_3$); ^{31}P NMR (162.0 MHz, $CDCl_3$): $\delta = 36.0$ (d, $J(Rh,P) = 128.9$ Hz); elemental analysis (%) for $C_{31}H_{56}IP_2Rh$ (720.6): calcd: C 51.67, H 7.83; found: C 51.44, H 7.88.

Preparation of *trans*-[RhI{=C=C=C(*p*-$C_6H_4OMe)_2$}$(PiPr_3)_2$] (7): This compound was prepared as described for **5**, from **4** (78 mg, 0.11 mmol) and excess KI (500 mg, 3.01 mmol) as starting materials. Red crystalline solid; yield 75 mg (96%); m.p. 147 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 1880$ (ν(C=C=C)) cm^{-1}; ^1H NMR (400 MHz, C_6D_6): $\delta = 7.97$, 6.48 (both d, $J(H,H) = 8.8$ Hz, 4H each; C_6H_4), 3.17 (s, 6H; OCH_3), 3.10 (m, 6H; $PCHCH_3$), 1.37 (dvt, $N = 13.6$, $J(H,H) = 7.2$ Hz, 36H; $PCHCH_3$); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 233.5$ (br d, $J(Rh,C) = 17.1$ Hz; Rh=C=C=C), 219.6 (dt, $J(Rh,C) = 67.6$, $J(P,C) = 18.1$ Hz; Rh=C=C=C), 159.1 (s; *C*OMe), 148.2 (s; *ipso*-C_6H_4), 141.1 (s; Rh=C=C=*C*), 125.8, 115.6 (both s; C_6H_4), 54.9 (s; OCH_3), 26.0 (vt, $N = 19.9$ Hz; $PCHCH_3$), 20.7 (s; $PCHCH_3$); ^{31}P NMR (162.0 MHz, C_6D_6): $\delta = 35.1$ (d, $J(Rh,P) = 129.9$ Hz); elemental analysis (%) for $C_{35}H_{56}IO_2P_2Rh$ (800.6): calcd: C 52.51, H 7.05, Rh 12.85; found: C 52.22, H 6.91, Rh 12.90.

Preparation of *trans*-[Rh(OH)(=C=C=CPh_2)$(PiPr_3)_2$] (8): A solution of **1** (131 mg, 0.20 mmol) in a 10:1 mixture of C_6H_6–*t*BuOH (3 mL) was treated with *t*BuOK (27 mg, 0.24 mmol) and stirred for 1 h at room temperature. A change of color from red to dark green occurred. The solvent was removed in vacuo and the residue was extracted with diethyl ether (15 mL). After the extract was evaporated to dryness in vacuo, the remaining solid was dissolved in diethyl ether (4 mL) and the solution was stored at −20 °C for 30 h. A green microcrystalline solid precipitated which was separated from the mother liquor, washed with acetone (2 × 1 mL; −20 °C), and dried; yield 103 mg (82%); m.p. 138 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 3620$ (ν(OH)), 1880 (ν(C=C=C)) cm^{-1}; ^1H NMR (200 MHz, C_6D_6): $\delta = 7.91$, 7.46, 6.82 (all m, 10H; C_6H_5), 2.74 (m, 6H; $PCHCH_3$), 1.33 (dvt, $N = 13.4$, $J(H,H) = 7.0$ Hz, 36H; $PCHCH_3$), signal of OH not exactly located; ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 247.4$ (dt, $J(Rh,C) = 17.1$, $J(P,C) = 5.8$ Hz; Rh=C=C=C), 221.8 (dt, $J(Rh,C) = 51.8$, $J(P,C) = 18.2$ Hz; Rh=C=C=C), 154.8 (br s; *ipso*-C_6H_5), 129.7 (br s; Rh=C=C=*C*), 130.2, 126.0, 123.2 (all s; C_6H_5), 23.2 (vt, $N = 18.2$ Hz; $PCHCH_3$), 20.2 (s; $PCHCH_3$); ^{31}P NMR

(81.0 MHz, C_6D_6): $\delta = 40.8$ (d, J(Rh,P) = 143.0 Hz); elemental analysis (%) for $C_{33}H_{53}OP_2Rh$ (630.6): calcd: C 62.85, H 8.47, Rh 16.32; found: C 62.49, H 7.99, Rh 16.33. An alternative procedure for the preparation of **8** is as follows: A solution of **1** (123 mg, 0.19 mmol) in benzene (3 mL) was mixed with an aqueous solution of benzyltriethylammonium chloride (TEBA) in 40% NaOH (8 mL) and vigorously stirred for 2 h at room temperature. After the aqueous phase was separated, the organic phase was washed with water (3×5 mL), then treated with diethyl ether (5 mL), and dried with Na_2SO_4. The drying reagent was filtered and the filtrate was evaporated to dryness in vacuo. The remaining residue was dissolved in diethyl ether (5 mL) and the solution was stored at $-20\,^{\circ}C$ for 12 h. Green crystals precipitated which were washed with acetone (2×1 mL; $-20\,^{\circ}C$) and dried; yield 86 mg (72%).

Preparation of *trans*-[Rh(OH){=C=C=C(*o*-Tol)Ph}(P*i*Pr$_3$)$_2$] (9): This compound was prepared as described for **8**, from **2** (128 mg, 0.19 mmol) and *t*BuOK (27 mg, 0.24 mmol) as starting materials. Green microcrystalline solid; yield 107 mg (85%); m.p. 119 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 3620$ (ν(OH)), 1870 (ν(C=C=C)) cm^{-1}; ^{1}H NMR (200 MHz, C_6C_6): $\delta = 7.48$ (br m, 9H; C_6H_4 and C_6H_5), 2.67 (m, 6H; PC*H*CH$_3$), 2.07 (s, 3H; $C_6H_4CH_3$), 1.37 (dvt, $N = 13.4$, J(H,H) = 6.8 Hz, 36H; PCHCH_3), signal of OH not exactly located; ^{13}C NMR (50.3 MHz, C_6D_6): $\delta = 245.5$ (dt, J(Rh,C) = 12.1, J(P,C) = 5.7 Hz; Rh=C=*C*=C), 224.2 (dt, J(Rh,C) = 51.5, J(P,C) = 18.4 Hz; Rh=*C*=C=C), 153.6, 153.5 (both br s; *ipso*-C_6H_5 and *ipso*-C_6H_4Me), 131.3 (t, J(P,C) = 2.5 Hz; Rh=C=C=*C*), 131.7, 130.2, 128.3, 127.8, 127.0, 125.7, 124.6, 123.9, 119.9 (all s; C_6H_5 and C_6H_4), 23.1 (vt, $N = 18.4$ Hz; P*C*HCH$_3$), 20.2 (s; PCH*C*H$_3$), 19.9 (s; $C_6H_4CH_3$); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 40.8$ (d, J(Rh,P) = 142.5 Hz); elemental analysis (%) for $C_{34}H_{55}OP_2Rh$ (644.7): calcd: C 63.35, H 8.55; found: C 62.91, H, 8.55.

Preparation of *trans*-[Rh(OH){=C=C=C(*t*Bu)Ph}(P*i*Pr$_3$)$_2$] (10): This compound was prepared as described for **8**, from **3** (131 mg, 0.21 mmol) and KO*t*Bu (45 mg, 0.35 mmol) as starting materials. After recrystallization from pentane at $-78\,^{\circ}C$ dark green crystals were isolated; yield 117 mg (92%); m.p. 62 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 3635$ (ν(OH)), 1848 (ν(C=C=C)) cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.11$, 7.05, 6.90, (all m, 5H; C_6H_5), 2.55 (m, 6H; PC*H*CH$_3$), 1.28 (dvt, $N = 13.2$, J(H,H) = 6.0 Hz, 36H; PCHCH_3), 1.12 (s, 9H; C(CH_3)$_3$), signal of OH proton not exactly located; ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 240.9$ (dt, J(Rh,C) = 51.3, J(P,C) = 18.1 Hz; Rh=*C*=C=C), 234.1 (dt, J(Rh,C) = 13.1, J(P,C) = 7.0 Hz; Rh=C=*C*=C), 154.5 (br s; *ipso*-C_6H_5), 145.7 (br s; Rh=C=C=*C*), 126.8, 126.1, 120.0 (all s; C_6H_5), 49.9 (s; *C*(CH$_3$)$_3$), 25.1 (s; C(*C*H$_3$)$_3$), 22.9 (vt, $N =$ 18.1 Hz; P*C*HCH$_3$), 20.1 (s; PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, C_6D_6): $\delta =$ 41.0 (d, J(Rh,P) = 144.0 Hz); elemental analysis (%) for $C_{31}H_{57}OP_2Rh$ (610.7): calcd: C 60.97, H 9.41, Rh 16.85; found: C 60.57, H 9.42, Rh 17.54.

Preparation of *trans*-[Rh(OH){=C=C=C(*p*-C$_6$H$_4$OMe)$_2$}(P*i*Pr$_3$)$_2$] (11): This compound was prepared as described for **8**, from **4** (126 mg, 0.18 mmol) and KO*t*Bu (35 mg, 0.31 mmol) as starting materials. After recrystallization from diethyl ether at $-78\,^{\circ}C$ dark red crystals were isolated; yield 108 mg (86%); m.p. 83 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 3646$ (ν(OH)), 1862 (ν(C=C=C)) cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.94$, 6.52 (both d, J(H,H) = 8.8 Hz, 4H each; C_6H_4), 3.23 (s, 6H; OCH_3), 2.77 (m, 6H; PC*H*CH$_3$), 1.36 (dvt, $N = 13.6$, J(H,H) = 7.2 Hz, 36H; PCHCH_3), 1.16 (t, J(P,H) = 5.6 Hz, 1H; OH); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 237.7$ (dt, J(Rh,C) = 13.1, J(P,C) = 5.0 Hz; Rh=C=*C*=C), 221.7 (dt, J(Rh,C) = 52.3, J(P,C) = 18.1 Hz; Rh=*C*=C=C), 158.4 (s; *C*OMe), 147.9 (t, J(P,C) = 2.0 Hz; *ipso*-C_6H_4), 129.7 (s; Rh=C=C=*C*), 125.4, 115.2 (both s; C_6H_4), 54.8 (s; OCH_3), 23.2 (vt, $N = 18.0$ Hz; P*C*HCH$_3$), 20.2 (s; PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, C_6D_6): $\delta = 40.7$ (d, J(Rh,P) = 143.7 Hz); elemental analysis (%) for $C_{35}H_{57}O_3P_2Rh$ (690.7): calcd: C 60.87, H 8.32, Rh 14.90; found: C 60.94, H 8.09, Rh 14.18.

Preparation of *trans*-[Rh(OAc)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (12): A solution of **8** (96 mg, 0.15 mmol) in benzene (3 mL) was treated with acetic acid (14 μL, 0.27 mmol) and stirred for 1 h at room temperature. After the solvent was removed, the oily residue was dissolved in acetone (5 mL) and the solution was again evaporated to dryness. The remaining solid was recrystallized from acetone (3 mL) at $-20\,^{\circ}C$ to give green crystals which were separated from the mother liquor, washed with acetone (2×1 mL; $-20\,^{\circ}C$) and dried; yield 95 mg (94%); m.p. 93 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 1855$ (ν(C=C=C)), 1705 (ν(OCO_{asym})) cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 7.81$, 7.43, 6.79 (all m, 10H; C_6H_5), 2.67 (m, 6H; PC*H*CH$_3$), 1.94 (s, 3H; C(O)CH$_3$), 1.36 (dvt, $N = 13.4$, J(H,H) = 7.1 Hz, 36H; PCHCH_3); ^{13}C NMR (50.3 MHz, C_6D_6): $\delta = 245.0$ (dt, J(Rh,C) = 15.3, J(P,C) = 7.0 Hz; Rh=C=*C*=C), 204.8 (dt, J(Rh,C) = 66.8, J(P,C) = 17.8 Hz; Rh=*C*=C=C), 175.9 (s; *C*(O)CH$_3$), 154.4 (br t, J(P,C) = 2.5 Hz; *ipso*-C_6H_5), 134.8 (br t, J(P,C) = 2.5 Hz; Rh=C=C=*C*), 129.7, 126.5, 123.1 (all s; C_6H_5), 25.1 (s; C(O)*C*H$_3$), 24.4 (vt, $N = 18.4$ Hz; P*C*HCH$_3$), 20.2 (s; PCH*C*H$_3$); ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = 40.2$ (d, J(Rh,P) = 133.8 Hz): elemental analysis (%) for $C_{35}H_{55}O_2P_2Rh$ (672.7); calcd: C 62.49, H 8.24; found: C 62.28, H 8.06.

Preparation of *trans*-[Rh(OAc){=C=C=C(*o*-Tol)Ph}(P*i*Pr$_3$)$_2$] (13): This compound was prepared as described for **12**, from **9** (97 mg, 0.15 mmol) and acetic acid (14 μL, 0.27 mmol) as starting materials. Green microcrystalline solid; yield 93 mg (92%); m.p. 156 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 1875$ (ν(C=C=C)), 1710 (ν(OCO_{asym})) cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 7.47$ (br m, 9H; C_6H_4 and C_6H_5), 2.57 (m, 6H; PC*H*CH$_3$), 2.00 (s, 3H; $C_6H_4CH_3$), 1.98 (s, 3H; C(O)CH$_3$), 1.33 (dvt, $N = 13.4$, J(H,H) = 6.8 Hz, 36H; PCHCH_3); ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = 40.3$ (d, J(Rh,P) = 133.8 Hz); elemental analysis (%) for $C_{36}H_{57}O_2P_2Rh$ (686.7): calcd: C 62.97, H 8.37; found: C 62.81, H 8.26.

Preparation of *trans*-[Rh{OC(O)Ph}(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (14): This compound was prepared as described for **12**, from **8** (140 mg, 0.22 mmol) and benzoic acid (27 mg, 0.22 mmol) as starting materials. After recrystallization from ether at $-20\,^{\circ}C$ green crystals were obtained; yield 119 mg (73%); m.p. 137 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 1855$ (ν(C=C=C)), 1610 (ν(OCO_{asym})), 1340 (ν(OCO_{sym})) cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta =$ 8.28, 7.83, 7.42, 7.17, 6.78 (all m, 15H; C_6H_5), 2.63 (m, 6H; PC*H*CH$_3$), 1.33 (dvt, $N = 13.1$, J(H,H) = 6.9 Hz, 36H; PCHCH_3); ^{13}C NMR (50.3 MHz, C_6D_6): $\delta = 246.3$ (dt, J(Rh,C) = 15.9, J(P,C) = 7.0 Hz; Rh=C=*C*=C), 210.6 (dt, J(Rh,C) = 66.1, J(P,C) = 18.4 Hz; Rh=*C*=C=C), 171.0 (s, *C*(O)Ph), 154.4 (br t, J(P,C) = 2.5 Hz, *ipso*-C_6H_5); 136.4 (br t, J(P,C) = 2.9 Hz; Rh=C=C=*C*), 138.1, 130.3, 129.9, 127.8, 126.6, 123.2 (all s, C_6H_5), 24.4 (vt, $N = 18.4$ Hz; P*C*HCH$_3$), 20.2 (s; PCH*C*H$_3$); ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = 40.2$ (d, J(Rh,P) = 135.1 Hz); elemental analysis (%) for $C_{40}H_{57}O_2P_2Rh$ (734.7): calcd: C 65.39, H 7.82; found: C 65.43, H 8.00.

Preparation of *trans*-[Rh(OPh)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (15): A solution of **8** (135 mg, 0.21 mmol) in benzene (4 mL) was treated with phenol (20 mg, 0.21 mmol) and stirred for 10 min at room temperature. A change of color from green to dark brown occurred. The solvent was removed in vacuo, and the residue was extracted with acetone (8 mL). After the extract was concentrated to about 4 mL in vacuo, it was stored for 15 h at $-20\,^{\circ}C$. A black microcrystalline solid precipitated wich was separated from the mother liquor, washed with acetone (3×1 mL; $-20\,^{\circ}C$) and dried; yield 138 mg (91%); m.p. 127 °C; IR (C_6H_6): $\tilde{\nu} = 1865$ (ν(C=C=C)) cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 7.86$, 7.44, 7.31, 6.80, 6.72, 6.51 (all m, 15H; C_6H_5), 2.49 (m, 6H; PC*H*CH$_3$), 1.25 (dvt, $N = 13.4$, J (H,H) = 7.0 Hz, 36H; PCHCH_3); ^{13}C NMR (50.3 MHz, C_6D_6): $\delta = 251.6$ (dt, J(Rh,C) = 14.6, J(P,C) = 5.7 Hz; Rh=C=*C*=C), 229.8 (dt, J(Rh,C) = 59.1, J(P,C) = 18.4 Hz; Rh=*C*=C=C), 169.4 (br s; *ipso*-OC_6H_5), 154.4 (t, J(P,C) = 2.2 Hz; *ipso*-C_6H_5), 136.3 (t, J(P,C) = 2.2 Hz; Rh=C=C=*C*), 129.8, 129.0, 126.8, 123.6, 120.6, 113.8 (all s; C_6H_5), 24.0 (vt, $N = 18.4$ Hz; P*C*HCH$_3$), 20.2 (s; PCH*C*H$_3$); ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = 38.9$ (d, J(Rh,P) = 138.2 Hz); elemental analysis (%) for $C_{39}H_{57}OP_2Rh$ (706.7): calcd: C 66.28, H 8.13; found: C 65.92, H 7.94.

Preparation of *trans*-[Rh(OPh){=C=C=C(*o*-Tol)Ph}(P*i*Pr$_3$)$_2$] (16): This compound was prepared as described for **15**, from **9** (130 mg, 0.20 mmol) and phenol (19 mg, 0.20 mmol) as starting materials. Black microcrystalline solid; yield 117 mg (81%); m.p. 123 °C; IR (C_6H_6): $\tilde{\nu} = 1865$ (ν(C=C=C) cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 7.11$ (br m, 14H; C_6H_4 and C_6H_5), 2.46 (m, 6H; PC*H*CH$_3$), 2.03 (s, 3H; $C_6H_4CH_3$), 1.24 (dvt, $N =$ 13.4, J(H,H) = 7.0 Hz, 36H; PCHCH_3); ^{13}C NMR (50.3 MHz, C_6D_6): $\delta =$ 249.2 (dt, J(Rh,C) = 14.6, J(P,C) = 5.7 Hz; Rh=C=*C*=C), 230.5 (dt, J(Rh,C) = 58.5, J(P,C) = 19.1 Hz; Rh=*C*=C=C), 169.3 (br s; *ipso*-OC_6H_5), 154.4, 153.2 (both t, J(P,C) = 2.2 Hz; *ipso*-C_6H_4 and *ipso*-C_6H_5), 136.3 (t, J(P,C) = 2.9 Hz; Rh=C=C=*C*), 131.7, 130.4, 129.0, 128.8, 127.4, 126.8, 124.7, 124.2, 120.5, 120.0, 113.8 (all s; C_6H_4 and C_6H_5), 24.0 (vt, $N = 18.4$ Hz; P*C*HCH$_3$), 20.2 (s; PCH*C*H$_3$); ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = 39.1$ (d, J(Rh,P) = 137.9 Hz); MS (70 eV): m/z: 720 ([M^+]), 627 ([$M^+ -$ OPh]); elemental analysis (%) for $C_{40}H_{59}OP_2Rh$ (720.8): calcd: C 66.66, H 8.25; found: C 66.43, H 8.61.

Preparation of *trans*-[Rh(OTs)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (17): A solution of **8** (91 mg, 0.15 mmol) in THF (3 mL) was treated at $-20\,^{\circ}C$ dropwise with a 0.38 M solution of *p*-toluenesulfonic acid (TsOH) in THF (0.38 mL, 0.14 mmol) and, after warming, stirred for 30 min at room temperature.

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The solvent was removed in vacuo, the residue was washed with pentane (2×3 mL) and then dissolved in acetone (3 mL). After the solution was stored for 30 h at $-20\,^{\circ}$C, orange crystals precipitated which were separated from the mother liquor, washed with acetone (2×1 mL; $-20\,^{\circ}$C) and dried; yield 60 mg (55 %); m.p. 152 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 1880$ (ν(C=C=C)) cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 7.41$ (br m, 14H; C_6H_4 and C_6H_5), 2.51 (m, 6H; PC*H*CH_3), 2.32 (s, 3H; $C_6H_4CH_3$), 1.18 (dvt, $N = 13.5$, J (H,H) = 6.9 Hz, 36H; PCHCH_3); ^{13}C NMR (50.3 MHz, C_6D_6): $\delta = 245.0$ (dt, J(Rh,C) = 17.8, J(P,C) = 6.4 Hz; Rh=C=*C*=C), 237.6 (dt, J(Rh,C) = 68.2, J(P,C) 17.9 Hz; Rh=*C*=C=C), 152.9, 143.9, 139.4 (all s; *ipso*-C_6H_4 and *ipso*-C_6H_5), 144.1 (s; Rh=C=C=*C*), 129.8, 128.3, 127.8, 126.9, 124.3 (all s; C_6H_4 and C_6H_5), 24.6 (vt, $N = 19.1$ Hz; P*C*HCH$_3$), 21.1 ($C_6H_4CH_3$), 20.3 (s; PCH*C*H$_3$); ^{31}P NMR (81.0 MHz, $CDCl_3$): $\delta = 41.5$ (d, J(Rh,P) = 133.7 Hz); elemental analysis (%) for $C_{40}H_{59}O_3P_2SRh$ (784.8): calcd: C 61.21, H 7.58; found: C 60.83, H 7.86.

Preparation of *trans*-[Rh(OTs){=C=C=C(*o*-Tol)Ph}(P*i*Pr$_3$)$_2$] (18): This compound was prepared as described for **17**, from **9** (90 mg, 0.14 mmol) and a 0.38 M solution of TsOH in THF (0.38 mL, 0.14 mmol) as starting materials. Orange crystals; yield 65 mg (61 %); m.p. 141 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 1880$ (ν(C=C=C)) cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 8.01$, 7.64, 7.02, 6.87, 6.71 (all m, 13H; C_6H_4 and C_6H_5), 2.70 (m, 6H; PC*H*CH_3), 1.98, 1.94 (both s; 3H each, $C_6H_4CH_3$), 1.27 (dvt, $N = 13.7$, J (H,H) = 7.1 Hz, 36H; PCHCH_3); ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = 41.4$ (d, J(Rh,P) = 133.4 Hz); elemental analysis (%) for $C_{41}H_{61}O_3P_2SRh$ (798.9): calcd: C 61.64, H 7.70, N 4.01; found: C 60.80, H 7.51, N 4.20.

Preparation of *trans*-[Rh(OTs)(CO)(P*i*Pr$_3$)$_2$] (19): A slow stream of CO was passed for 30 s through a solution of **17** (75 mg, 0.10 mmol) in benzene (3 mL) at 10 °C. A stepwise change of color from orange to green and finally to light yellow occurred. After the solution was stirred for 5 min at room temperature, the solvent was removed in vacuo, the oily residue was dissolved in acetone (2 mL) and the solution was stored for 30 h at $-30\,^{\circ}$C. Light orange crystals precipitated which were separated from the mother liquor, washed acetone (3×1 mL; $-20\,^{\circ}$C) and dried; yield 48 mg (81 %); m.p. 119 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 1945$ (ν(CO)) cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.95$, 6.86 (both m, 4H; C_6H_4), 2.74 (m, 6H; PC*H*CH_3), 1.97 (s, 3H; $C_6H_4CH_3$), 1.23 (dvt, $N = 14.1$, J(H,H) = 7.2 Hz, 36H; PCHCH_3); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 191.2$ (dt, J(Rh,C) = 77.7, J(P,C) = 16.3 Hz; RhCO), 143.7 (s; *ipso*-C_6H_4), 139.8, 128.6, 126.8 (all s; C_6H_4), 25.0 (vt, $N = 20.2$ Hz; P*C*HCH$_3$); 21.1 (s; $C_6H_4CH_3$), 20.2 (s; PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, C_6D_6): $\delta = 51.3$ (d, J(Rh,P) = 119.1 Hz); elemental analysis (%) for $C_{26}H_{49}O_4P_2RhS$ (622.6): calcd: C 50.16, H 7.93; found: C 50.70, H 7.91.

Preparation of *trans*-[Rh(C≡CPh$_2$OAc)(CO)(P*i*Pr$_3$)$_2$] (20): A slow stream of CO was passed for 30 s through a solution of **12** (95 mg, 0.14 mmol) in benzene (3 mL) at 10 °C. A stepwise change of color from orange to green and finally to light yellow occurred. After the solution was stirred for 5 min at room temperature, the solvent was removed in vacuo, the remaning yellow solid was washed with acetone (3×2 mL; $-20\,^{\circ}$C) and dried; yield 89 mg (90 %); m.p. 116 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 2100$ (ν(C≡C)), 1950 (ν(CO)), 1750 (ν(C=O)) cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 7.64$, 7.15, 7.04 (all m, 10H; C_6H_5), 2.43 (m, 6H; PC*H*CH_3), 1.78 (s, 3H; C(O)CH_3), 1.25 (dvt, $N = 13.8$, J(H,H) = 7.3 Hz, 36H; PCHCH_3); ^{13}C NMR (50.3 MHz, C_6D_6): $\delta = 196.2$ (dt, J(Rh,C) = 59.1, J(P,C) = 14.0 Hz; RhCO), 167.2 (s; *C*(O)CH$_3$), 145.6 (s; *ipso*-C_6H_5), 127.7, 127.6, 127.0 (all s; C_6H_5), 125.5 (dt, J(Rh,C) = 42.6, J(P,C) = 20.3 Hz; Rh*C*≡C), 114.2 (dt, J(Rh,C) = 12.1, J(P,C) = 2.5 Hz; RhC≡*C*), 81.7 (s; RhC≡C-*C*), 26.0 (vt, $N = 21.6$ Hz; P*C*HCH$_3$), 21.8 (s; C(O)*C*H$_3$), 20.4 (s; PCH*C*H$_3$); ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = 55.3$ (d, J(Rh,P) = 126.4 Hz); elemental analysis (%) for $C_{37}H_{57}O_3P_2Rh$ (700.7); calcd: C 61.17, H 7.91; found: C 61.35, H 7.90.

Preparation of *trans*-[Rh{C≡CPh(*o*-Tol)OAc}(CO)(P*i*Pr$_3$)$_2$] (21): This compound was prepared as described for **20**, from **13** (98 mg, 0.14 mmol) and CO as starting materials. Yellow microcrystalline solid; yield 89 mg (89 %); m.p. 116 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 1945$ (ν(CO)), 1745 (ν(C=O)) cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 8.16$, 7.54, 7.08 (all m, 9H; C_6H_4 and C_6H_5), 2.42 (m, 6H; PC*H*CH_3), 2.21 (s, 3H; $C_6H_4CH_3$), 1.77 (s, 3H; C(O)CH_3), 1.25 (dvt, $N = 13.7$, J(H,H) = 7.1 Hz, 18H; PCHCH_3), 1.24 (dvt, $N = 13.4$, J(H,H) = 7.1 Hz, 18H; PCHCH_3); ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = 55.5$ (d, J(Rh,P) = 126.4 Hz); elemental analysis (%) for $C_{37}H_{57}O_3P_2Rh$ (714.7): calcd: C 62.18, H 8.04; found: C 61.81, H 8.01.

Preparation of *trans*-[Rh(C≡CPh$_2$OPh)(CO)(P*i*Pr$_3$)$_2$] (22): This compound was prepared as described for **20**, from **15** (85 mg, 0.12 mmol) and CO as starting materials. Yellow microcrystalline solid; yield 80 mg (79 %); m.p. 136 °C; IR (C_6H_6): $\tilde{\nu} = 1940$ (ν(CO)) cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.81$, 7.10, 6.72 (all m, 15H; C_6H_5), 2.03 (m, 6H; PC*H*CH_3), 1.18 (dvt, $N = 13.5$, J(H,H) = 7.1 Hz, 36H; PCHCH_3); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 196.2$ (dt, J(Rh,C) = 58.5, J(P,C) = 14.0 Hz; RhCO), 157.2, 146.7 (both s; *ipso*-C_6H_5), 128.7, 128.0, 127.8, 127.1, 120.4, 119.1 (all s; C_6H_5), 127.0 (dt, J(Rh,C) = 43.1, J(P,C) = 20.6 Hz; Rh*C*≡C), 114.8 (dt, J(Rh,C) = 12.2, J(P,C) = 3.0 Hz; RhC≡*C*), 82.3 (s; RhC≡C-*C*)), 26.1 (vt, $N = 21.4$ Hz; P*C*HCH$_3$), 20.4 (s; PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, C_6D_6): $\delta = 54.9$ (d, J(Rh,P) = 125.9 Hz); MS (70 eV): m/z 734 ([M^+]), 641 ([M^+ − OPh]); elemental analysis (%) for $C_{40}H_{57}O_2P_2Rh$ (734.7); calcd: C 65.39, H 7.82; found: C 65.05, H 8.18.

Preparation of *trans*-[Rh{C≡CPh(*o*-Tol)OPh}(CO)(P*i*Pr$_3$)$_2$] (23): This compound was prepared as described for **20**, from **16** (97 mg, 0.13 mmol) and CO as starting materials. Yellow microcrystalline solid; yield 80 mg (79 %); m.p. 136 °C; IR (C_6H_6): $\tilde{\nu} = 1940$ (ν(CO)) cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 8.52$, 7.67, 7.30, 7.12 (all m, 14H; C_6H_4 and C_6H_5), 2.39 (m, 6H; PC*H*CH_3), 2.29 (s, 3H; $C_6H_4CH_3$), 1.24 (dvt, $N = 13.8$, J(H,H) = 7.2 Hz, 18H; PCHCH_3), 1.23 (dvt, $N = 13.7$, J(H,H) = 7.1 Hz, 18H; PCHCH_3); ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = 54.3$ (d, J(Rh,P) = 126.5 Hz); elemental analysis (%) for $C_{41}H_{59}O_2P_2Rh$ (748.8): calcd: C 65.77, H 7.94; found: C 65.14, H 7.38.

Preparation of *trans*-[Rh(CN)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (24): A slow stream of freshly generated HCN was passed for 30 s through a solution of **8** (62 mg, 0.10 mmol) in benzene (3 mL) at room temperature. A rapid change of color from dark green to dark red occurred. After the solution was stirred for 5 min, the solvent was evaporated in vacuo, the residue was dissolved in acetone (3 mL) and the solution stored for 12 h at $-20\,^{\circ}$C. Red crystals precipitated which were separated from the mother liquor, washed with acetone (2×1 mL; $-20\,^{\circ}$C) and dried; yield 57 mg (91 %); m.p. 152 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 2100$ (ν(CN)), 1880 (ν(C=C=C)) cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 7.91$, 7.46, 6.75 (all m, 10H; C_6H_5), 2.81 (m, 6H; PC*H*CH_3), 1.34 (dvt, $N = 13.7$, J(H,H) = 7.1 Hz, 36H; PCHCH_3); ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = 45.1$ (d, J(Rh,P) = 130.4 Hz).

Preparation of *trans*-[Rh{C≡CPh$_2$CH(CN)$_2$}(CO)(P*i*Pr$_3$)$_2$] (25): A solution of **8** (85 mg, 0.14 mmol) in benzene (3 mL) was treated dropwise with a 0.36 M solution of $CH_2(CN_2)$ in benzene (0.38 mL, 0.14 mmol) at room temperature. A rapid change of color from green to blue occured. After about 15 s a slow stream of CO was passed through the solution for 30 s which led again to a change of color from blue to yellow. The solution was stirred for 15 min and the solvent was evaporated in vacuo. The residue was dissolved in benzene (2 mL), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 10 cm). With benzene, a yellow fraction was eluted which was brought to dryness in vacuo. The remaining yellow solid was dissolved in pentane (4 mL) and the solution was stored at $-78\,^{\circ}$C for 12 h. Yellow crystals precipitated which were separated from the mother liquor, washed with pentane (2×1 mL; $-20\,^{\circ}$C) and dried; yield 86 mg (90 %); m.p. 152 °C; IR (KBr): $\tilde{\nu} = 2253$ (ν(CN)), 2081 (ν(C≡C)), 1935 (ν(CO)) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.35$ (m, 10H; C_6H_5), 4.58 (s, 1H; $CH(CN)_2$), 2.43 (m, 6H; PC*H*CH_3), 1.24 (dvt, $N = 14.0$, J(H,H) = 7.2 Hz, 36H; PCHCH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 195.2$ (dt, J(Rh,C) = 58.4, J(P,C) = 14.1 Hz; RhCO), 141.4 (s; *ipso*-C_6H_5), 128.2, 127.8, 127.6 (all s; C_6H_5), 126.7 (dt, J(Rh,C) = 44.3, J(P,C) = 20.1 Hz; Rh*C*≡C), 112.4 (s; CH(*C*N)$_2$), 111.8 (dt, J(Rh,C) = 13.1, J(P,C) = 3.0 Hz; RhC≡*C*), 53.7 (s; RhC≡C−*C*), 36.8 (s; *C*H(CN)$_2$), 25.8 (vt, N = 21.4 Hz; P*C*HCH$_3$), 20.4 (s; PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 53.5 (d, J(Rh,P) = 126.0 Hz); elemental analysis (%) for $C_{37}H_{53}N_2OP_2Rh$ (706.7): calcd: C 62.88, H 7,56; N, 3.96; found: C 62.59, H 7.62, N, 3.83.

Preparation of *trans*-[Rh{C≡CPh(*t*Bu)CH(CN)$_2$}(CO)(P*i*Pr$_3$)$_2$] (26): This compound was prepared as described for **25**, from **10** (112 mg, 0.18 mmol) and a 0.36 M solution of $CH_2(CN)_2$ in benzene (0.51 mL, 0.18 mmol) as starting materials. Yellow solid; yield 94 mg (88 %); m.p. 123 °C; IR (KBr): $\tilde{\nu} = 2253$ (ν(CN)), 2077 (ν(C≡C)), 1946 (ν(CO)) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.38$ (m, 5H; C_6H_5), 4.46 (s, 1H; $CH(CN)_2$), 2.66 (m, 6H; PC*H*CH_3), 1.34 (dvt, $N = 14.4$, J(H,H) = 7.2 Hz, 18H; PCHCH_3), 1.33 (dvt, $N = 14.4$, J(H,H) = 7.6 Hz, 18H; PCHCH_3), 1.03 (s, 9H; C(CH_3)$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 194.6 (dt, J(Rh,C) = 58.4, J(P,C) = 15.1 Hz; RhCO), 139.0 (s; *ipso*-C_6H_5), 129.2, 127.4, 126.9 (all s; C_6H_5), 123.2 (dt, J(Rh,C) = 45.3, J(P,C) = 19.1 Hz; Rh*C*≡C), 114.0, 113.8

(both s; $CH(CN)_2$), 111.0 (d, J(Rh,C) = 13.1 Hz; RhC≡*C*), 57.7 (s; RhC≡*C*-*C*), 39.5 (s; *C*H(CN)$_2$), 32.1 (s; *C*(CH$_3$)$_3$), 27.6 (s; C(*C*H$_3$)$_3$), 26.1 (vt, N = 21.2 Hz; P*C*HCH$_3$), 20.3 (s; PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 53.9 (d, J(Rh,P) = 125.4 Hz); MS (70 ev): m/z: 686 ([M^+]), 658 ([M^+ − CO]), 593 ([M^+ − CO − CH(CN)$_2$]); elemental analysis (%) for $C_{35}H_{57}N_2OP_2Rh$ (686.7): calcd: C 61.22, H 8.37, N 4.08; found: C 60.99, H 8.40, N 3.87.

Preparation of *trans*-[Rh{C≡CC(*p*-C$_6$H$_4$OMe)$_2$CH(CN)$_2$}(CO)(P*i*Pr$_3$)$_2$] (27): This compound was prepared as described for **25**, from **11** (95 mg, 0.14 mmol) and a 0.36 M solution of $CH_2(CN)_2$ in benzene (0.38 mL, 0.14 mmol) as starting materials. Yellow solid; yield 86 mg (82%); m.p. 140 °C; IR (KBr): $\tilde{\nu}$ = 2252 (ν(CN)), 2088 (ν(C≡C)), 1943 (ν(CO)) cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.41, 6.47 (both d, J(H,H) = 8.8 Hz, 4H each; C$_6$H$_4$), 4.01 (s, 1H; CH(CN)$_2$), 3.30 (s, 6H; OCH$_3$), 2.45 (m, 6H; PC*H*CH$_3$), 1.27 (dvt, N = 14.0, J(H,H) = 7.2 Hz, 36H; PCHC*H*$_3$); ^{13}C NMR (100.6, C_6D_6): δ = 195.8 (dt, J(Rh,C) = 58.4, J(P,C) = 15.1 Hz; RhCO), 159.4 (s; *C*OMe), 141.5 (s; *ipso*-C$_6$H$_4$), 129.4, 113.7 (both s; C$_6$H$_4$), 124.8 (dt, J(Rh,C) = 43.3, J(P,C) = 20.1 Hz; RhC≡C), 113.3 (s; CH(*C*N)$_2$), 113.2 (dt, J(Rh,C) = 12.1, J(PC) = 4.0 Hz; RhC≡*C*), 54.8 (s; OCH$_3$), 53.2 (s; RhC≡C−*C*), 37.2 (s; *C*H(CN)$_2$), 26.1 (vt, N = 21.5 Hz; P*C*HCH$_3$), 20.4 (s; PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, C_6D_6): δ = 54.0 (d, J(Rh,P) = 125.4 Hz); MS (70 ev): m/z: 766 ([M^+]), 673 ([M^+ − CO − CH(CN)$_2$]); elemental analysis (%) for $C_{39}H_{57}N_2O_3P_2Rh$ (766.8): calcd: C 61.09, H 7.49, N 3.65; found: C 61.53, H 7.80, N 3.65.

Preparation of *trans*-[Rh{C≡CCPh$_2$CH(CN)$_2$}(CNMe)(P*i*Pr$_3$)$_2$] (28): A solution of **8** (78 mg, 0.12 mmol) in benzene (3 mL) was treated dropwise with a 0.36 M solution of $CH_2(CN)_2$ in benzene (0.35 mL, 0.12 mmol) at room temperature. A rapid change of color from green to blue occurred. After about 15 s, a 0.05 M solution of CNMe in benzene (2.9 mL, 0.13 mmol) was added dropwise which led again to a change of color from blue to yellow. The solution was stirred for 5 min und worked up analogously as described for **25**. Yellow solid; yield 77 mg (86%); m.p. 120 °C (decomp); IR (KBr): $\tilde{\nu}$ = 2240 (ν(CN)), 2080 (ν(C≡C)), 2045 (ν(CN)) cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.32 (m, 10H; C$_6$H$_5$), 4.13 (s, 1H; CH(CN)$_2$), 2.47 (m, 6H; PC*H*CH$_3$), 2.23 (s, 3H; CNCH$_3$), 1.37 (dvt, N = 13.6, J(H,H) = 7.2 Hz, 36H; PCHC*H*$_3$); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 163.3 (dt, J(Rh,C) = 53.3, J(P,C) = 16.1 Hz; *C*NCH$_3$), 142.9 (s; *ipso*-C$_6$H$_5$), 130.4 (dt, J(Rh,C) = 44.3, J(P,C) = 20.1 Hz; RhC≡C), 128.4, 128.2, 127.4 (all s; C$_6$H$_5$), 113.3 (s; CH(*C*N)$_2$), 110.3 (d, J(Rh,C) = 12.1 Hz; RhC≡*C*), 54.3 (s; RhC≡C−*C*), 37.1 (s; *C*H(CN)$_2$), 28.2 (s; CN*C*H$_3$), 25.8 (vt, N = 19.1 Hz; P*C*HCH$_3$), 20.6 (s; PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, C_6D_6): δ = 52.8 (d, J(Rh,P) = 133.5 Hz); elemental analysis (%) for $C_{38}H_{56}N_3P_2Rh$ (719.7): calcd: C 63.41, H 7.84, N 5.84; found: C 63.29, H 7.48, N 5.70.

Preparation of *trans*-[Rh{C≡CCPh(*t*Bu)CH(CN)$_2$}(CNMe)(P*i*Pr$_3$)$_2$] (29): This compound was prepared as described for **28**, from **10** (106 mg, 0.17 mmol), a 0.36 M solution of $CH_2(CN)_2$ in benzene (0.48 mL, 0.17 mmol) and a 0.05 M solution of CNMe in benzene (3.6 mL, 0.18 mmol) as starting materials. Yellow solid; yield 85 mg (92%); m.p. 84 °C (decomp); IR (KBr): $\tilde{\nu}$ = 2253 (ν(CN)), 2090 (ν(C≡C)), 2045 (ν(CN)) cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.32 (m, 5H; C$_6$H$_5$), 3.94 (s, 1H; CH(CN)$_2$), 2.67 (m, 6H; PC*H*CH$_3$), 2.21 (s, 3H; CNCH$_3$), 1.44 (dvt, N = 13.6, J(H,H) = 6.8 Hz, 18H; PCHC*H*$_3$), 1.42 (dvt, N = 13.6, J(H,H) = 6.8 Hz, 18H; PCHC*H*$_3$), 1.02 (s, 9H; C(CH$_3$)$_3$); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 163.1 (dt, J(Rh,C) = 52.3, J(P,C) = 16.1 Hz; *C*NCH$_3$), 140.4 (s; *ipso*-C$_6$H$_5$), 129.9, 127.3, 127.0 (all s; C$_6$H$_5$) 126.9 (dt, J(Rh,C) = 44.3, J(P,C) = 19.1 Hz; RhC≡C), 114.7 (s; CH(*C*N)$_2$), 109.4 (d, J(Rh,C) = 12.1 Hz; RhC≡*C*), 58.0 (s; RhC≡C−*C*), 39.7 (s; *C*H(CN)$_2$), 32.7 (s; *C*(CH$_3$)$_3$), 28.3 (s; CN*C*H$_3$), 28.0 (s; C(*C*H$_3$)$_3$), 26.0 (vt, N = 19.1 Hz; P*C*HCH$_3$), 20.7 (s; PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, C_6D_6): δ = 53.0 (d, J(Rh,P) = 133.3 Hz); elemental analysis (%) for $C_{36}H_{60}N_3P_2Rh$ (699.8): calcd: C 61.79, H 8.64, N, 6.01; found: C 61.51, H 8.37, N 5.91.

Preparation of *trans*-[Rh{C≡CC(*p*-C$_6$H$_4$OMe)$_2$CH(CN)$_2$}(CNMe)(P*i*Pr$_3$)$_2$] (30): This compound was prepared as described for **28**, from **11** (105 mg, 0.15 mmol), a 0.36 M solution of $CH_2(CN)_2$ in benzene (0.42 mL, 0.15 mmol) and a 0.05 M solution of CNMe in benzene (3.2 mL, 0.16 mmol) as starting materials. Yellow solid; yield 90 mg (75%); m.p. 93 °C (decomp); IR (KBr): $\tilde{\nu}$ = 2170 (ν(CN)), 2097 (ν(C≡C)), 2058 (ν(CNMe)) cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.53, 6.77 (both d, J(H,H) = 8.8 Hz, 4H each; C$_6$H$_4$), 4.16 (s, 1H; CH(CN)$_2$), 3.31 (s, 6H; OCH$_3$), 2.45 (m, 6H; PC*H*CH$_3$), 2.22 (s, 3H; CNCH$_3$), 1.35 (dvt, N = 13.6, J(H,H) = 7.2 Hz, 36H; PCHC*H*$_3$); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 163.4 (dt, J(Rh,C) = 53.3, J(P,C) = 16.1 Hz; *C*NCH$_3$), 159.3 (s; *C*OMe), 135.2 (s; *ipso*-*C*$_6$H$_4$), 129.7, 113.6 (both s; C$_6$H$_4$), 129.2 (dt, J(Rh,C) = 50.3, J(P,C) = 20.1 Hz; RhC≡*C*), 113.3 (s; CH(*C*N)$_2$), 111.3 (br d, J(Rh,C) = 12.1 Hz; RhC≡C), 54.8 (s; OCH$_3$), 53.3 (s; RhC≡C?*C*), 37.6 (s; *C*H(CN)$_2$), 28.2 (s; CN*C*H$_3$), 25.8 (vt, N = 19.2 Hz; P*C*HCH$_3$), 20.6 (s; PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, C_6D_6): δ = 52.9 (d, J(Rh,P) = 133.6 Hz); elemental analysis (%) for $C_{40}H_{60}N_3O_2P_2Rh$ (789.9); calcd: C 61.83, H 8.93, N 4.05; found: C 61.46, H 8.59, N 3.89.

Reaction of compound 25 with HCl: A solution of **25** (60 mg, 0.08 mmol) in CH_2Cl_2 (3 mL) was treated at −60 °C with a 0.17 M solution of HCl in benzene (0.55 mL, 0.09 mmol). After the solution was stirred for about 2 min, the solvent was removed in vacuo. The residue was extracted with pentane (3 mL, −20 °C) and the extract was evaporated to dryness in vacuo. The pale yellow residue was characterized spectroscopically as a mixture of HC≡CCPh$_2$CH(CN)$_2$ (**31**) and *trans*-[RhCl(CO)(P*i*Pr$_3$)$_2$] (**33**). Data for **31**: IR (CH_2Cl_2): $\tilde{\nu}$ = 3300 (ν(≡CH)), 2135 (ν(C≡C)) cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.45 (m, 4H; C$_6$H$_5$), 7.33 (m, 6H; C$_6$H$_5$), 4.96 (s, 1H; CH(CN)$_2$), 3.02 (s, 1H; C≡CH); ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 138.6 (s; *ipso*-C$_6$H$_5$), 129.4, 129.3, 127.4 (all s; C$_6$H$_5$), 111.7 (s; CN), 82.0 (s; *C*≡CH), 79.0 (s; C≡*C*H), 58.5 (s; C≡C−*C*), 36.3 (s; *C*H(CN)$_2$).

Reation of compound 26 with HCl: This was carried out analogously as described above with **26** (68 mg, 0.10 mmol) and a 0.17 M solution of HCl in benzene (0.64 mL, 0.11 mmol) as starting materials. A mixture of HC≡CCPh(*t*Bu)CH(CN)$_2$ (**32**) and **33** was obtained. Data for **32**: IR (CH_2Cl_2): $\tilde{\nu}$ = 3300 (ν(≡CH)), 2244 (ν(CN)), 2148 (ν(C≡C)) cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.58 (m, 2H; C$_6$H$_5$), 7.43 (m, 3H; C$_6$H$_5$), 4.61 (s, 1H; CH(CN)$_2$), 3.00 (s, 1H; C≡CH), 1.14 (s, 9H; CH$_3$); ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 136.3 (s; *ipso*-C$_6$H$_5$), 129.0, 128.7, 128.5 (all s; C$_6$H$_5$), 113.0, 112.9 (both s; CN), 81.9 (s; *C*≡CH), 78.8 (s; C≡*C*H), 56.2 (s; C≡C−*C*), 39.4 (s; *C*H(CN)$_2$), 32.1 (s; *C*(CH$_3$)$_3$), 27.4 (s; C(*C*H$_3$)$_3$).

X-ray crystal structure determination of compound 22: Single crystals were grown from an acetone/acetonitrile mixture at 0 °C. Crystal data (from 23 reflections, $10° < \Theta < 13°$): monoclinic, space group $P2_1/c$ (no. 14); a = 12.819(4), b = 14.633(3), c = 21.020(7) Å, β = 92.36(2)°, V = 3940(2) Å^3, Z = 4, ρ_{calcd} = 1.239 g cm^{-3}, μ(Mo$_{K\alpha}$) = 0.142 cm^{-1}, T = 293 K; crystal size 0.10 × 0.15 × 0.56 mm; Enraf-Nonius CAD 4 diffractometer, Mo$_{K\alpha}$ radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 15.4); $\vartheta/2\Theta$ scan, max 2Θ = 48.00°; 6477 reflections measured, 6167 independent reflections, 4328 regarded as being observed [$F_o > 2\sigma(Fo)$]; intensity data were corrected for Lorentz and polarization effects, minimum transmission was 96.44%. The structure was solved by direct methods (SHELXS-86);[24] atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares (418 parameters, SHELXL-93).[25] 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 = 0.0368, wR_2 = 0.0899; reflex/parameter ratio 10.35; residual electron density +0.400/-0.305 e Å^{-3}.
Ref. code NACSAL, *Cambridge Structural Database System*, **2000**.

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