# Rhodium(I) and Rhodium(III) Complexes Formed by Coordination and C–H Activation of Bulky Functionalized Phosphanes

**Giuseppe Canepa, Carsten D. Brandt, Kerstin Ilg, Justin Wolf, and Helmut Werner*[a]**

*Dedicated to Professor Manfred Weidenbruch on the occasion of his 65th birthday*

**Abstract:** The reaction of $[\{RhCl(C_8H_{14})_2\}_2]$ (**2**) with $iPr_2PCH_2CH_2C_6H_5$ ($L^1$) led, via the isolated dimer $[\{RhCl(C_8H_{14})(L^1)\}_2]$ (**3**), to a mixture of three products **4a–c**, of which the dinuclear complex $[\{RhCl(L^1)_2\}_2]$ (**4a**) was characterized by X-ray crystallography. The mixture of **4a–c** reacts with CO, ethene, and phenylacetylene to give the square-planar compounds *trans*-$[RhCl(L)(L^1)_2]$ (L = CO (**5**), $C_2H_4$ (**6**), C=CHPh (**9**)). The corresponding allenylidene(chloro) complex *trans*-$[RhCl(=C=C=CPh_2)(L^1)_2]$ (**11**), obtained from **4a–c** and $HC\equiv CC(OH)Ph_2$ via *trans*-$[RhCl\{=C=CHC(OH)Ph_2\}(L^1)_2]$ (**10**), could be converted stepwise to the related hydroxo, cationic aqua, and cationic acetone derivatives **12**—**14**, respectively. Treatment of **2** and $[\{RhCl(C_2H_4)_2\}_2]$ (**7**) with two equivalents of $tBu_2PCH_2CH_2C_6H_5$ ($L^2$) gave the dimers $[\{RhCl(C_8H_{14})(L^2)\}_2]$ (**15**) and $[\{RhCl(C_2H_4)(L^2)\}_2]$ (**16**), which both react with $L^2$ in the molar ratio of 1:2 to afford the five-coordinate aryl(hydrido)rhodium(III) complex $[RhHCl(C_6H_4CH_2CH_2PtBu_2\text{-}\kappa^2C,P)(L^2)]$ (**17**) by C–H activation. The course of the reactions of **17** with CO, $H_2$, PhC≡CH, HCl, and $AgPF_6$, leading to the compounds **19–21**, **24**, and **25a**, respectively, indicate that the coordinatively unsaturated isomer of **17** with the supposed composition $[RhCl(L^2)_2]$ is the reactive species. Labeling experiments using $D_2$, DCl, and PhC≡CD support this proposal. With either $[Rh(C_8H_{14})(\eta^6\text{-}L^2\text{-}\kappa P]PF_6$ or $[Rh(C_2H_4)(\eta^6\text{-}L^n\text{-}\kappa P]PF_6$ ($n = 1$ and 2) as the starting materials, the corresponding halfsandwich-type complexes **27**, **28**, and **32** were obtained. The nonchelating counterpart of the dihydrido compound **32** with the composition $[RhH_2(PiPr_3)(\eta^6\text{-}C_6H_6)]PF_6$ (**35**) was prepared stepwise from $[Rh(C_2H_4)(PiPr_3)(\eta^6\text{-}C_6H_6)]PF_6$ and $H_2$ in acetone via the tris(solvato) species $[RhH_2(PiPr_3)(acetone)_3]PF_6$ (**34**) as intermediate. The synthesis of the bis(chelate) complex $[Rh(\eta^4\text{-}C_8H_{12})(C_6H_5OCH_2CH_2PtBu_2\text{-}\kappa^2O,P)]BF_4$ (**39**) is also described. Besides **4a**, the compounds **17**, **25a**, and **39** have been characterized by X-ray crystal structure analysis.

**Keywords:** arene complexes · C–H activation · hydrido complexes · phosphane complexes · rhodium

## Introduction

The bis(triisopropylphosphane)rhodium(I) compound $[\{RhCl(PiPr_3)_2\}_2]$ (**1**) is probably one of the most reactive rhodium(I) compounds known to date.[1] It reacts not only with $H_2$, $O_2$, $N_2$, CO, and $C_2H_4$ but also with terminal alkynes to give stepwise π-alkyne-, alkynyl(hydrido)-, and vinylidenerhodium derivatives.[2] By a similar route, allenylidene as well as pentatetraenylidenerhodium(I) complexes have been obtained.[3, 4]

While there is no doubt that **1** is a chloro-bridged dimer in the crystal, we argued on the basis of molecular weight determinations[5] that in dilute solutions the corresponding monomer $[RhCl(PiPr_3)_2]$, probably being the reactive species toward $H_2$, $O_2$, $N_2$ etc., is generated. We therefore set out to prepare a related mononuclear complex by using a partly chelating, hemilabile phosphane such as $iPr_2PCH_2CH_2OMe$ and indeed succeeded with the isolation (and structural characterization) of $[RhCl(iPr_2PCH_2CH_2OMe\text{-}\kappa P)(iPr_2PCH_2CH_2OMe\text{-}\kappa^2O,P)]$ at low temperatures.[6] Moreover, the high reactivity of this molecule, which is fluxional in solution, prompted us to find out whether also bulky phosphanes having a benzene ring as the functional group in the side chain would behave in the same way.

In a recent article, we have described the synthesis and derivatization of the new phosphanes $iPr_2P(CH_2)_nC_6H_5$ ($n = 2$ and 3) and $tBu_2P(CH)_2C_6H_5$ as well as the preparation of some halfsandwich-type complexes derived thereof.[7] Herein we summarize our work on mono- and dinuclear rhodium compounds with four- and five-coordinate rhodium centers containing the beforementioned phosphanes mainly *P*-bonded. The most surprising result is the easy and reversible C–H activation of the substituted phenyl group of the ligands $R_2P(CH_2)_2C_6H_5$ (R = *i*Pr, *t*Bu) providing a new possibility to

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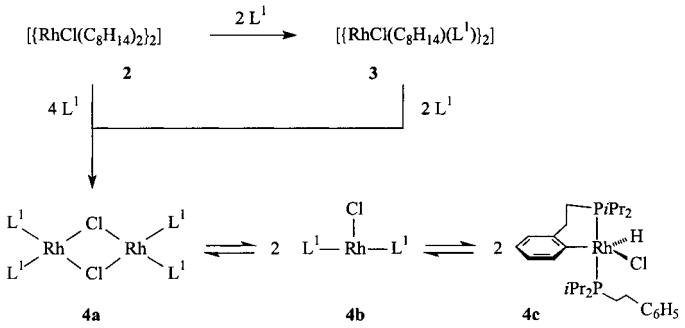
stabilize an in situ generated 14-electron species $[RhCl(PR_2X)_2]$. A preliminary communication has already appeared.[8]

## Results and Discussion

**Rhodium complexes obtained with $i$Pr$_2$PCH$_2$CH$_2$C$_6$H$_5$ (L$^1$) as the substrate**: Under conditions similar to those used for the preparation of **1**, the reaction of $[\{RhCl(C_8H_{14})_2\}_2]$ (**2**) with a twofold excess of L$^1$ in pentane at room temperature results in the formation of a yellow solid, the analytical composition of which corresponds to **3** (Scheme 1). The product is thermally not exceedingly stable and decomposes in solution (benzene or dichloromethane) at 10 °C in a few hours. The $^{31}$P NMR spectrum, which displays a doublet at $\delta = 53.5$ ppm with a $^{31}$P – $^{103}$Rh coupling constant of 184.8 Hz, confirms the stereochemical equivalence of the phosphane ligands.




Scheme 1. L$^1$ = $i$Pr$_2$PCH$_2$CH$_2$C$_6$H$_5$.

Treatment of **2** with four instead of two equivalents of L$^1$ leads to the formation of a red solution from which, after removal of the solvent and recrystallization from pentane at low temperature, a red air-sensitive solid can be isolated. Although the elemental analysis of the solid is in agreement with a ratio of Rh:Cl:L$^1$ = 1:1:2, the $^1$H and $^{31}$P NMR spectra indicate that the product is probably a mixture of three species but not solely a rhodium(I) complex containing two intact phosphane ligands L$^1$ per metal atom. The $^{31}$P NMR spectrum, measured immediately after the solid has been dissolved in $C_6D_6$, displays a sharp doublet at $\delta = 51.2$ ppm with $J(^{31}P,^{103}Rh) = 198.4$ Hz, which by comparison with **1** is assigned to the dimer **4a** (Scheme 1). Already after a few minutes (at room temperature), further signals appear and after 3–4 h an equilibrium state is established. Besides **4a**, a second compound **4c** is present, the $^1$H NMR spectrum of which shows in the high-field region a signal at $\delta = -19.89$ ppm being typical for a hydridorhodium species. The signal is split into a doublet of doublets of doublets due to one $^1$H – $^{103}$Rh and two $^1$H – $^{31}$P couplings. The obvious assumption that two inequivalent phosphane ligands must be coordinated to the metal, is supported by the appearance of two doublets of doublets in the $^{31}$P NMR spectrum with a difference in the chemical shift of about 20 ppm. The whole set of NMR data for **4c** is comparable to that of the analogous complex **17** (see Scheme 4) which has been characterized by X-ray crystallography.

The third species observed in solution possibly is the monomer **4b**. It is characterized by a doublet resonance in the $^{31}$P NMR spectrum at $\delta = 48.2$ ppm with a $^{31}$P – $^{103}$Rh coupling constant of 195.8 Hz. That **4b** is a monomeric compound is supported by the comparison with the $^{31}$P NMR spectrum of the $PCy_3$ counterpart $[RhCl(PCy_3)_2]$ which also displays a signal at $\delta = 48.2$ ppm with $J(^{31}P,^{103}Rh) = 207.5$ Hz.[9] Therefore, it seems that **4b** is a 14-electron monomer that can not only be stabilized by dimerization but also by intramolecular C – H activation, the latter being a reversible process. We note that both by dimerization and intramolecular C – H activation the molecule approaches a situation in which each rhodium center formally possesses a 16-electron count.

Single crystals of the dinuclear complex **4a** were grown from a saturated solution in pentane at −60 °C and were studied by X-ray structure analysis (Figure 1). The molecule has a center of inversion in the midpoint of the Rh1-Cl1-Rh1A-Cl1A rhombohedron which is strictly planar. The distances Rh1–Cl1 and Rh1A–Cl1A are almost identical. The torsional angles Rh1A-Cl1-Rh1-P1 and Rh1A-Cl1-Rh1-P2 are 7.5(3)° and 175.66(5)°, respectively. They deviate slightly from the ideal 0° and 180° values, probably as a result of steric hindrance between the bulky substituents at the phosphorus atoms.

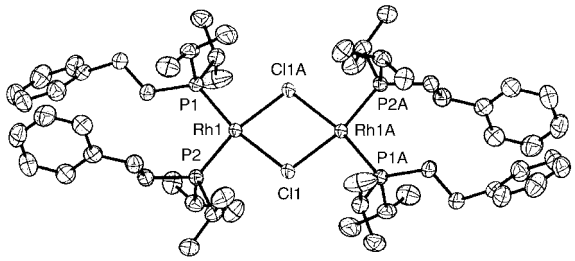


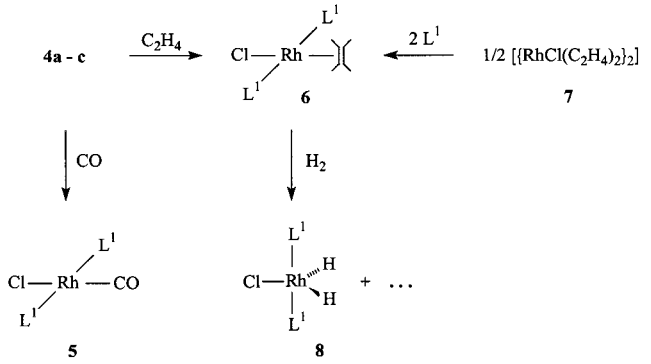

Figure 1. Molecular structure of **4a**. Principal bond lengths [Å] and angles [°] (with estimated standard deviations in parentheses): Rh1–P1 2.2436(8), Rh1–P2 2.2286(8), Rh1–Cl1 2.4365(9), Rh1–Cl1A 2.4224(9); Cl1-Rh1-Cl1A 77.39(3), P1-Rh1-P2 101.72(3), P1-Rh1-Cl1 168.07(3), P1-Rh1-Cl1A 90.78(3), P2-Rh1-Cl1 89.95(3), P2-Rh1-Cl1A 166.63(3).

The assumption that the compounds **4a** and **4c** are in equilibrium with the monomer **4b** is supported by the reactivity of the solution containing the mixture of **4a**, **4b**, and **4c** with various substrates. Passing a slow stream of CO through the red solution generates the carbonyl complex **5**, which precipitates as a light yellow, air-stable solid and has been isolated in 86% yield. Characteristic spectroscopic features of **5** (Scheme 2) are the two doublets of virtual triplets for the PCHC$H_3$ protons in the $^1$H NMR and the strong ν(CO) band at 1942 cm$^{-1}$ in the IR spectrum.

A similar reaction as that leading to **5** occurs if the red solution is treated with $C_2H_4$. The corresponding ethene derivative **6** is formed as a yellow solid and has been identified by elemental analysis and spectroscopic techniques. It can equally be prepared from the dimer **7** upon treatment with L$^1$.

The ethene derivative **6** reacts with $H_2$ to give mainly (ca. 90%) the dihydride **8**. Since attempts to remove the by-




Scheme 2. $L^1 = iPr_2PCH_2CH_2C_6H_5$.

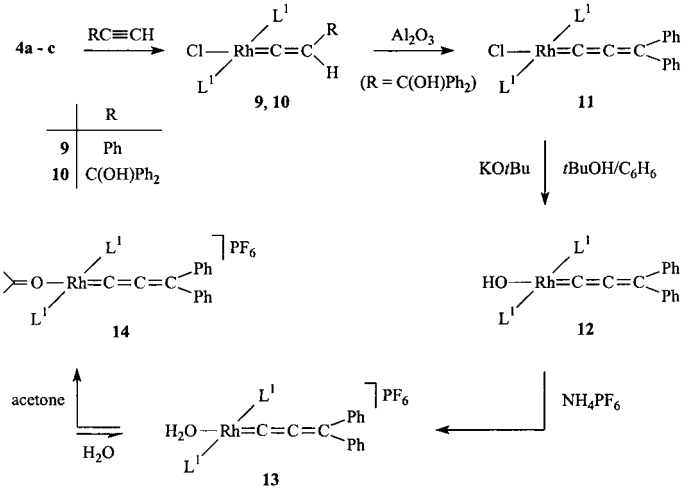
products by fractional crystallization failed, the dihydrido compound has been characterized spectroscopically. The $^1$H NMR spectrum of **8** displays a doublet of triplets at $\delta = -21.62$ ppm for the hydrido ligands, and the $^{31}$P NMR spectrum a sharp doublet at $\delta = 52.1$ ppm, confirming the equivalence of the phosphane ligands. In agreement with the results of the X-ray crystal structure analyses of [$RhH_2Cl(PiPr_3)_2$][10] and [$RhH_2Cl(PtBu_3)_2$][11] we assume that the geometry of **8** corresponds to a trigonal bipyramid.

The reactions of **4a–c** with phenylacetylene and the propargylic alcohol HC≡CC(OH)$Ph_2$ proceed similarly to those with CO and $C_2H_4$. Treating the red solution with the corresponding terminal alkyne HC≡CR in toluene at room temperature leads initially to a change of color from red to yellow and after 8–12 h from yellow to dark blue (R = Ph) or brown (R = C(OH)$Ph_2$). After removal of the solvent and chromatographic workup or extraction of the residue with pentane blue-violet or green mycrocrystalline solids with the analytical composition corresponding to **9** and **10** (Scheme 3) were isolated in 69–75% yield. Typical spectroscopic data of **9** and **10** are the signal for the Rh=C=CH proton at $\delta = 1.66$ ppm (**9**) or $\delta = 1.40$ ppm (**10**) in the $^1$H NMR spectra and the two low-field resonances for the vinylidene carbon atoms at $\delta = 296.5$ and 112.2 ppm (**9**) or $\delta = 286.4$ and 118.6 ppm (**10**) in the $^{13}$C NMR spectra. Based on earlier observations,[12] we interpret the initial change of color from red to yellow as indicative for the formation of an ($\eta^2$-alkyne)rhodium(I) or an alkynyl(hydrido)rhodium(III) intermediate.

The conversion of **10** to the allenylidene complex **11** followed the methodology which we had already applied for the bis(triisopropylphosphane) counterpart.[3a] Treatment of a solution of **10** in benzene with acidic $Al_2O_3$ leads to a change of color from green to orange-red and affords, using the well-known workup procedure,[3a, 13] the product as an orange air-stable solid in 83% yield. The IR spectrum of **11** shows a strong ν(C=C=C) stretch at 1879 cm$^{-1}$, and the $^{13}$C NMR spectrum shows three resonances for the allenylidene carbon atoms at $\delta = 245.6$ ($C_\beta$), 223.3 ($C_\alpha$) and 154.3 ppm ($C_\gamma$), respectively. The fact that in each of the $^1$H, $^{13}$C, and $^{31}$P NMR spectra of **11** only one set of signals for the hydrogen, carbon, and phosphorus atoms of the phosphane ligands is observed, is consistent with the assumption that the barrier for rotation around the Rh–C bond is rather small on the NMR time scale.

In contrast to some hydroxorhodium(I) compounds such as [{Rh($\mu$-OH)($PiPr_3$)$_2$}$_2$] and *trans*-[Rh(OH)(=C=CHPh)($PiPr_3$)$_2$] that were prepared from the corresponding chloro derivatives and NaOH under biphasic conditions,[14] the related complex **12** was obtained from **11** and KO*t*Bu in a mixture of benzene and *tert*-butyl alcohol. The isolated yield of the brown microcrystalline solid is 59%. The presence of the hydroxo ligand is shown both by the strong absorption at 3642 cm$^{-1}$ in the IR spectrum and by the triplet resonance at $\delta = 1.57$ ppm in the $^1$H NMR spectrum. The chemical shifts for the signals of the allenylidene carbon atoms in the $^{13}$C NMR spectrum of **12** are quite similar to those of **11**, thus supporting the idea that the *trans* influence of the chloro and hydroxo ligands is of comparable magnitude.

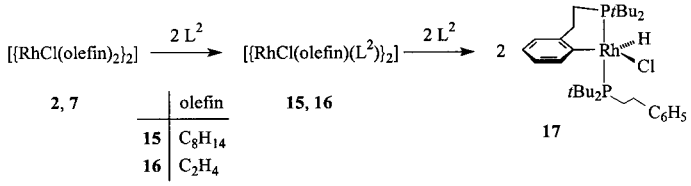
In attempting to labilize the position *trans* to the allenylidene unit and create the possibility to generate via elimination of one group $L^1$ a halfsandwich-type cation [Rh(=C=C=C$Ph_2$)($\eta^6$-$C_6H_5CH_2CH_2PiPr_2$-$\kappa P$)]$^+$, the hydroxo ligand of compound **12** was stepwise substituted for acetone. Protonation of **12** with $NH_4PF_6$ in acetone at −78 °C leads initially to an intermediate, which is characterized by a doublet at $\delta = 33.7$ ppm (with $J(^{31}P,^{103}Rh) = 132.3$ Hz) in the $^{31}$P NMR spectrum. Upon warming the solution to room temperature, a red compound is formed, which, based on the elemental analysis, the conductivity, and the spectroscopic data, is the acetone derivative **14** (Scheme 3). While the $^1$H NMR spectra of **14** and the intermediate are rather similar, in the $^{31}$P NMR spectrum of **14** the doublet resonance is shifted by 3 ppm upfield compared with that of the intermediate. Since the latter is partly regenerated by dissolving **14** in aqueous acetone, we assume that the species initially formed in the protonation of **12** with $NH_4PF_6$ is the aquarhodium(I) complex **13**. In the presence of excess acetone, the equilibrium between **13** and **14** is shifted towards the acetone derivative, which has been isolated as a red air-sensitive solid in 71% yield. Various attempts to abstract one phosphane ligand $L^1$ and to transform **14** to the above-mentioned halfsandwich-type cation by using either $N_2O$ (to generate the oxophosphorane $iPr_2P(O)CH_2CH_2C_6H_5$) or a phosphane-accepting transition-metal compound such as




Scheme 3. $L^1 = iPr_2PCH_2CH_2C_6H_5$.

CuCl or $[PdCl_2(NCPh)_2]$ remained unsuccessful. It should be mentioned that quite recently the counterpart of **14** with P*i*Pr$_3$ instead of L$^1$ as the phosphane has been prepared from *cis*-$[Rh(acetone)_2(P{i}Pr_3)_2]PF_6$ and HC≡CC(OH)Ph$_2$ as the starting materials.[15]

**Rhodium complexes obtained with *t*Bu$_2$PCH$_2$CH$_2$C$_6$H$_5$ (L$^2$) as the substrate**: The more bulky functionalized phosphane L$^2$ behaves in some respects similarly, but in others differently, compared with L$^1$. Thus, while treatment of the olefinic starting material **2** with two equivalents of L$^2$ gives the expected chloro-bridged dimer **15** (the analogue of **3**), the reaction of **2** with four equivalents of L$^2$ does not lead to a mixture of products but affords the aryl(hydrido)rhodium(III) complex **17** exclusively (Scheme 4). This species formed by an




Scheme 4. L$^2$ = *t*Bu$_2$PCH$_2$CH$_2$C$_6$H$_5$.

intramolecular C–H activation can also be prepared stepwise from $[RhCl(C_2H_4)_2]_2$ (**7**) and excess L$^2$ via the monosubstitution product **16** as the intermediate. Compound **17** is a yellow solid which is much less air-sensitive than **1** or the mixture of **4a**, **4b** and **4c**. The characteristic spectroscopic features of **17** are the hydride resonance at $\delta = -18.11$ ppm in the $^1$H NMR specrum, the signal for the metal-bonded carbon atom of the six-membered ring at $\delta = 146.9$ ppm in the $^{13}$C NMR spectrum, and the two doublets of doublets at $\delta = 65.7$ and 43.0 ppm in the $^{31}$P NMR spectrum. According to a two-dimensional P,H correlation spectrum, the $^{31}$P NMR resonance at lower field belongs to the phosphorus atom of the chelating ligand and that at higher field to that of the purely *P*-bonded phosphane. With the same technique, the signals for the protons and carbon atoms of the different methylene and methyl groups of the ligands have been assigned.

The result of the X-ray crystal structure analysis of **17** is shown in Figure 2. The coordination geometry around the rhodium center corresponds to a distorted trigonal bipyramid with the two phosphorus atoms in the apical positions. The position of the hydrido ligand could not be exactly located and had been calculated with a Rh–H distance of 1.5 Å. The two Rh–P bond lengths are slightly longer than in the related, more symmetrical chelate complex [RhHCl-(*t*Bu$_2$PCH$_2$C$_6$H$_3$CH$_2$P*t*Bu$_2$-$\kappa^3$*P*,*C*,*P*)] (**18**) obtained from $RhCl_3 \cdot 3H_2O$ and 1.5-C$_6$H$_4$(CH$_2$P*t*Bu$_2$)$_2$ in 2-propanol/water under reflux.[16] In contrast, the Rh–C31 bond length of **17** (1.967(5) Å) is slightly shorter than in **18** (1.999(7) Å) and in the related hydrido and methyl complexes [RhHCl{CH(CH$_2$CH$_2$P*t*Bu$_2$)$_2$-$\kappa^3$*P*,*C*,*P*}] (2.082(2) Å)[17] and [RhCH$_3$Cl{*t*Bu$_2$PCH$_2$C$_6$H-3.5-(CH$_3$)$_2$CH$_2$P*t*Bu$_2$-$\kappa^3$*P*,*C*,*P*}] (2.02(2) Å),[18] respectively. The P1-Rh-P2 axis of **17** is significantly bent (160.18(5)°), which could be due both to steric hindrance between the phosphane substituents and the

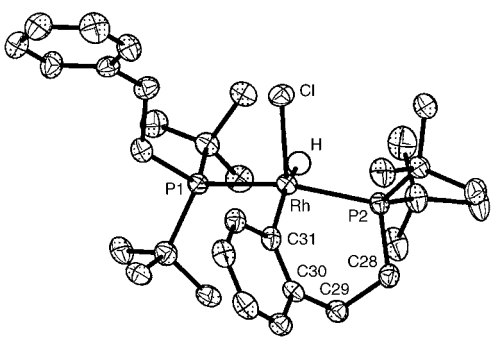
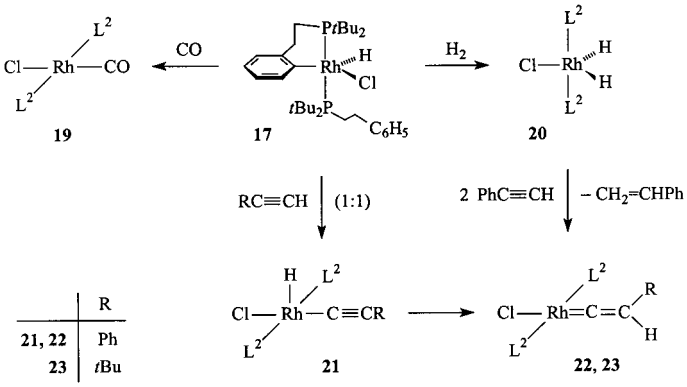



Figure 2. Molecular structure of **17**. Principal bond lengths [Å] and angles [°] (with estimated standard deviations in parentheses); the position of the metal-bonded hydrogen has been calculated: Rh–P1 2.3746(14), Rh–P2 2.3344(13), Rh–Cl 2.4687(13), Rh–C31 1.967(5), C30–C31 1.407(7), C29–C30 1.510(7), C28–C29 1.535(6), P2–C28 1.830(5); P1-Rh-P2 160.18(5), P1-Rh-C31 96.89(13), P1-Rh-Cl 98.01(5), P2-Rh-C31 87.54(13), P2-Rh-Cl 99.74(5), C31-Rh-Cl 103.40(14), Rh-P2-C28 110.62(15), Rh-C31-C30 126.8(4), C31-C30-C29 121.1(4), C30-C29-C28 109.0(4), P2-C28-C29 113.8(3).

strain of the chelate ring. The conformation of this six-membered ring corresponds to a boat form, the rhodium and the carbon atom C29 being the top and the end of the boat.

The two dinuclear compounds **15** and **16** (Scheme 4), formed as intermediates in the reactions of **2** and **7** with L$^2$, have also been isolated and analytically characterized. Both are yellow, air-stable solids which are readily soluble in common organic solvents. By comparing the reactivity of the ligands L$^1$ and L$^2$ towards the bis(ethene)chloro complex **7**, the remarkable difference is that two of the smaller phosphanes L$^1$ are able to coordinate to a rhodium(I) center to give **6**, while the interaction of a second molecule of the more bulky phosphane L$^2$ does not only lead to elimination of ethene but also to a rapid cyclometalation reaction.

The results regarding the reactivity of **17** toward CO, H$_2$, and terminal alkynes are summarized in Scheme 5. They all proceed under mild conditions (25 °C, 1 bar) and give the products in good (**22**, **23**) to excellent yields (**19**, **20**). The carbonyl complex (a yellow air-stable solid with a ν(CO) stretch at 1937 cm$^{-1}$) is noteworthy insofar as the NMR spectra indicate that in contrast to analogues such as *trans*-$[RhCl(CO)(P{i}Pr_3)_2]$[1a] and *trans*-$[RhCl(CO)(P{i}Pr_2Ph)_2]$[19] the molecule is fluxional in solution. In the $^1$H and $^{13}$C as well as in the $^{31}$P NMR spectrum the signals are rather broad at 293 K




Scheme 5. L$^2$ = *t*Bu$_2$PCH$_2$CH$_2$C$_6$H$_5$.

but sharpen after increasing the temperature. At 343 K in [$D_8$]toluene, the $^{13}C$ NMR spectrum of **19** displays a clean doublet of triplets at $\delta = 190.2$ ppm for the carbon nuclei of the carbonyl group and the $^{31}P$ NMR spectrum a slightly broadened doublet at $\delta = 57.8$ ppm for the apparently equivalent phosphane ligands. However, upon cooling the sample this doublet broadens and at 223 K three sets of signals for the $^{31}P$ phosphorus atoms are observed. One of these sets corresponds to the AB portion of an ABX spectrum and two to the $A_2$ portion of two $A_2X$ spectra, where A and B are $^{31}P$ and X is $^{103}Rh$, respectively. Each of the subspectra represents a rotational isomer of **19** and is a local minimum on the energy surface. The three rotamers $R^1$, $R^2$, and $R^3$ (Figure 3) differ by the orientation of the phosphane sub-

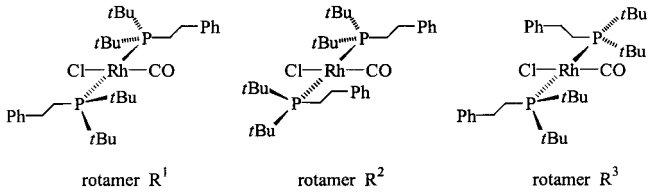



Figure 3. Proposed conformations for the three rotamers of **19**.

stituents along the P-Rh-P axis, thereby the most bulky *tert*-butyl groups probably playing the dominant role. The common feature of $R^1$, $R^2$, and $R^3$ is that the *t*Bu units are always oriented above and below the plane formed by the Rh, Cl, CO, and P atoms which makes the phosphane ligands equivalent in $R^2$ and $R^3$ but not in $R^1$. Therefore, $R^1$ gives rise to two doublets of doublets, whereas for $R^2$ and $R^3$ one doublet for each (with different intensities) is observed. In $R^2$ the alkyl chain $CH_2CH_2Ph$ has a transoid position to chloride and since this ligand, according to the Tolman concept, has a larger cone angle (102°) than CO (95°),[20] $R^2$ could be favored compared to $R^3$. We note that a related fluxional behavior in solution has been detected for the compounds *trans*-[RhCl(CO)(P*t*Bu$_2$R)$_2$] (R = H, Me Et, *n*Pr, *n*Bu, Ph)[21] as well as for the halfsandwich-type complexes [($\eta^6$-arene)OsR$_2$(PH*t*Bu$_2$)] (R = H, Me),[22] and in both cases has also been studied by $^{31}P$ NMR spectroscopy.

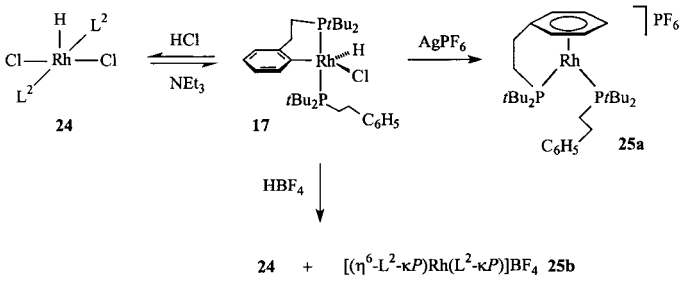
A dynamic behavior can also be observed for the vinylidene complex **22** (see Scheme 5), being prepared from **17** and phenylacetylene in toluene at room temperature. The $^{31}P$ NMR spectrum of **22** shows at 308 K a sharp doublet at $\delta =$ 52.5 ppm, at 293 K a broadened singlet at $\delta = 45.7$ ppm, and at 233 K three subspectra at $\delta = 47.7$ and 41.6 ppm (both dd) for rotamer $R^1$, at $\delta = 46.2$ (d) for rotamer $R^2$, and at $\delta = 41.8$ ppm (d) for rotamer $R^3$. The ratio of the three rotamers is not as much different as in the case of the carbonyl compound **19**. If the $^{31}P$ NMR spectrum of **22** is measured below 233 K, also the subspectra become broadened which we attribute to a freezing of the rotation around the Rh–C bond. In a similar way as **22**, the counterpart **23** with a *tert*-butyl instead of a phenyl substituent at the vinylidene unit has been obtained from **17** and *t*BuC≡CH and isolated as a blue-violet solid in 82% yield.

The alkynyl(hydrido)rhodium(III) derivative **21**, formed as an intermediate in the reaction of **17** with phenylacetylene, can be clearly detected by $^1H$ and $^{31}P$ NMR spectroscopy if the reaction is monitored at −78 °C in [$D_8$]toluene. The $^{31}P$ NMR spectrum of **21** displays a sharp doublet at $\delta = 40.5$ ppm with a $^{31}P-^{103}Rh$ coupling constant of 119.5 Hz. In the corresponding $^1H$ NMR spectrum, the hydride resonance appears at $\delta = -27.72$ ppm as a doublet of triplets with $J(P,H) = 11.6$ and $J(Rh,H) = 42.2$ Hz. These data are nearly identical with those of the compound [RhHCl(C≡CPh)(P*i*Pr$_3$)$_2$], which is less labile than **21** and for which a square-pyramidal structure has been proposed.[12a]

The C–H metalation of $L^2$ leading to the aryl(hydrido) fragment of **17** is not only reversed by treatment of **17** with CO or PhC≡CH but also if a suspension of **17** in pentane is stirred in the presence of $H_2$ at room temperature. Under these conditions, the dihydrido complex **20** is formed and, after evaporation of the solvent, isolated as a light yellow, slightly air-sensitive and thermally quite stable solid in 93% yield. Similarly to the more labile counterpart **8** (see Scheme 2) it exhibits a doublet of triplets for the Rh–H protons at $\delta = -22.63$ in the $^1H$ NMR spectrum in the high-field region and a doublet at $\delta = 65.6$ in the $^{31}P$ NMR spectrum. This indicates that the hydrido as well as the phosphane ligands are stereochemically equivalent. In solution, a dynamic behavior of **20** cannot be detected. Treatment of **17** with $D_2$ affords exclusively the bis(deuterio) derivative [RhD$_2$Cl(L$^2$)$_2$] which supports the assumption that not **17** but the coordinatively unsaturated isomer [RhCl(L$^2$)$_2$] is the reactive species.

The dihydrido complex **20** reacts with phenylacetylene to afford **22**. In this case, two equivalents of the alkyne are needed because one behaves as the trapping reagent for the two hydrides to form styrene. Since attempts to detect an intermediate such as [RhCl(L$^2$)$_2$] or possibly **17** failed, we assume that the addition of the alkyne to [RhCl(L$^2$)$_2$] (formed by abstraction of $H_2$ from **20**) is much faster than the C–H activation, this providing a hint about the energy of activation for the two different processes.

**Preparation of halfsandwich-type complexes with $L^1$ and $L^2$ as ligands**: The possibility that, by abstracting the hydride or the chloro ligand from **17**, a cation of composition [RhX(C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-$\kappa P$)(C$_6$H$_4$CH$_2$CH$_2$P*t*Bu$_2$-$\kappa^2 C,P$)]$^+$ (X = Cl, H) could be generated, prompted us to study also the reactivity of the cyclometalated complex **17** toward acids and $AgPF_6$. An almost instantaneous reaction of **17** takes place with gaseous HCl which does not lead, however, to the elimination of $H_2$ but instead to the addition of the substrate to the rhodium center. The dichloro(hydrido) compound **24** is formed as an orange air-stable solid that in the presence of triethylamine in $C_6D_6$ regenerates the precursor quantitatively (Scheme 6). Regarding the structure of **24**, we assume that in analogy to the structures of [RhHCl$_2$(P*i*Pr$_3$)$_2$] and [RhHCl$_2$(P*n*Pr$_2$*t*Bu)$_2$], determined crystallographically,[10, 23] it corresponds to a square pyramid and not to a trigonal bipyramid. This proposal is indirectly supported by the observation that the resonances for the protons and carbon atoms of the C(CH$_3$)$_3$ groups are broadened in the $^1H$ and $^{13}C$ NMR spectra at 293 K, while they become sharp at 333 K. Moreover, if the $^{31}P$ NMR spectrum of **24** is measured at




Scheme 6. $L^2 = tBu_2PCH_2CH_2C_6H_5$.

243 K, two signals at $\delta = 47.3$ and 46.6 ppm instead of one signal at $\delta = 47.9$ ppm (at 293 K) appear, the $^{31}P-^{103}Rh$ coupling constant in each case being 96.6 Hz. Thus it is possible that analogously to **19** and the rhodium vinylidenes **22** and **23** also for the monohydrido complex **24** two rotamers exist in which the positions of the *tert*-butyl groups and the alkyl chain differ along the P-Rh-P axis. By discussing this situation, one has to take into account that in **19**, **22**, and **23** as well as in **24** four ligands around the metal center possess a square-planar arrangement and therefore similar steric requirements result. Diagnostic for the presence of the hydrido ligand in **24** is the resonance in the $^1H$ NMR spectrum at $\delta = -30.84$ ppm which is split into a doublet of triplets due to $^1H-^{103}Rh$ and $^1H-^{31}P$ couplings. Treatment of **17** with DCl affords $[RhDCl_2(L^2)_2]$ and with PhC≡CD *trans*-$[RhCl(=C=CDPh)(L^2)_2]$, the deuterium being exclusively part of the vinylidene ligand.

The reaction of **17** with $HBF_4$ proceeds quite cleanly if one half equivalent of the acid is used. Two products are formed, one of which is the neutral hydridorhodium(III) compound **24** and the other the halfsandwich-type complex **25b** (see Scheme 6). This compound, which is a brownish air-stable solid with a decomposition temperature of 105 °C, has a cation with the formal composition $[Rh(L^2)_2]^+$ and is also accessible by chloride abstraction from **17**. Treatment of **17** with $AgPF_6$ in the molar ratio of 1:1 gives the corresponding $PF_6^-$ salt **25a**, the properties of which are very similar to those of **25b**. The $^{31}P$ NMR spectra of **25a** and **25b** confirm the unequal coordination of the two phosphane ligands and display two doublet of doublet resonances at $\delta = 81.5$ and 68.6 ppm (**25a**) and at $\delta = 80.1$ and 67.2 ppm (**25b**), respectively. On the basis of a two-dimensional P–H NMR correlation spectrum, the signal at lower field can be assigned to the phosphorus atom of the chelating ligand and the other to the phosphorus atom of the monodentate phosphane. We note that in contrast to the similar $PPh_2$-containing complex $[(\eta^6\text{-}p\text{-}FC_6H_4CH_2CH_2CH_2PPh_2\text{-}\kappa P)Rh(p\text{-}FC_6H_4CH_2CH_2CH_2\text{-}PPh_2\text{-}\kappa P)]BF_4$ reported by Mirkin et al.,[24] the NMR spectra of **25a** and **25b** are not temperature-dependent and thus a fluxional behavior in solution can be excluded.

The molecular structure of **25b** is shown in Figure 4. Similarly to the cyclooctene compound $[Rh(C_8H_{14})(\eta^6\text{-}L^1\text{-}\kappa P)]PF_6$,[7] the arene ring possesses a slightly inverse boat conformation with the characteristic feature that the *ipso*-carbon atom C1 and, to a smaller extent, the carbon atom C4 are bent toward the metal center. Due to the strain of the chelate ring, the distance Rh–C1 is significantly shorter than

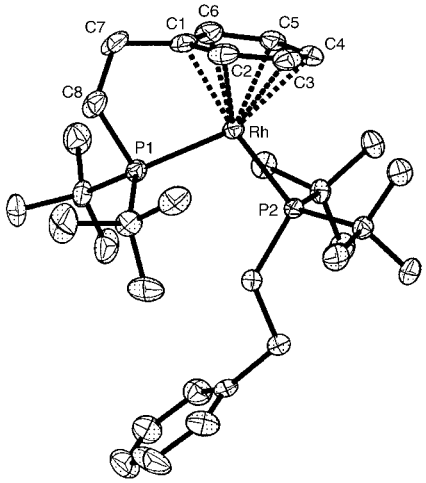
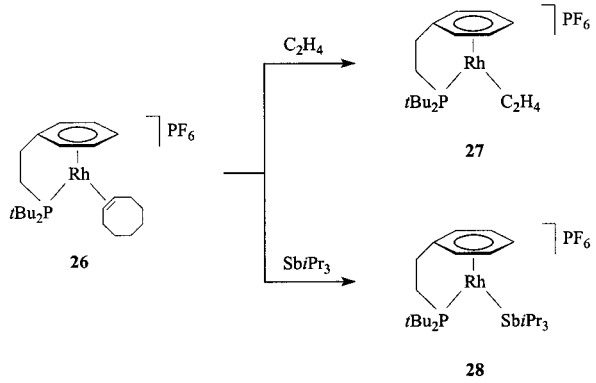



Figure 4. Molecular structure of **25b**. Principal bond lengths [Å] and angles [°] (with estimated standard deviations in parentheses): Rh–P1 2.3480(8), Rh–P2 2.3493(8), Rh–C1 2.246(3), Rh–C2 2.301(3), Rh–C3 2.375(2), Rh–C4 2.333(2), Rh–C5 2.367(3), Rh–C6 2.356(3); P1-Rh-P2 106.78(3), Rh-P1-C8 101.94(9), P1-C8-C7 115.08(19), C8-C7-C1 109.5(2).

the distances between rhodium and the other ring carbon atoms. The bond lengths Rh–P1 and Rh–P2, which are practically identical, are about 0.1 Å longer than in the structurally analogous complexes $[(\eta^6\text{-}RC_6H_4XCH_2CH_2PPh_2\text{-}\kappa P)Rh(RC_6H_4XCH_2CH_2PPh_2\text{-}\kappa P)]BF_4$ (R = H, $C_5H_4FeC_5H_5$; X = $CH_2$, O) with less bulky substituents at the phosphorus atoms.[24, 25] Compared with these compounds, the bond angle P1-Rh-P2 of **25b** is about 10° larger which could also be a consequence of the steric requirements of the *tert*-butyl groups.

Relatives of the halfsandwich-type complex **25a** with $C_2H_4$ and $SbiPr_3$ instead of monodentate $L^2$ are accessible by ligand substitution reactions of the cyclooctene derivative **26** (Scheme 7). The replacement of $C_8H_{14}$ by ethene or triisopropylstibane occurs rather slowly, probably due to the fact that the metal center in the 18-electron starting material is well shielded. To obtain the ethene complex **27** in good yields, it is necessary to remove the displaced cyclooctene almost completely which is done stepwise as described in the Experimental Section. Both **27** and **28** are thermally stable solids which are moderately air-sensitive and readily soluble in polar organic solvents. The $^1H$ NMR spectrum of **27** in

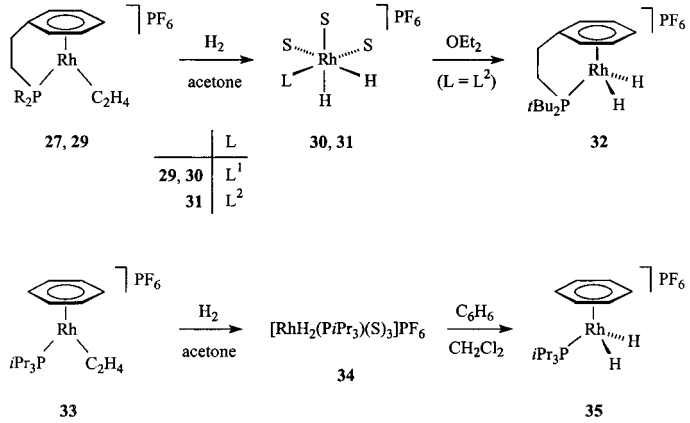



Scheme 7.

$[D_6]$acetone displays at room temperature only one signal (broadened singlet) for the ethene protons at $\delta = 3.22$ ppm indicating that under these conditions the rotation of the olefin around the $Rh-C_2H_4$ axis is quite fast. This is in agreement with earlier observations regarding the analogous compound $[Rh(\eta^6\text{-}C_6H_5CH_2CH_2P\textit{i}Pr_2\text{-}\kappa P)(C_2H_4)]PF_6$ (**29**), where the rotation is frozen at 230 K.[7]

The conversion of the ethene derivative **27** to the cationic dihydridorhodium(III) compound **32** proceeds stepwise. Stirring a solution of **27** in acetone for 12 h under a hydrogen atmosphere leads to a smooth change of color from orange-red to brown and, after crystallization from acetone/ether, yields a light brown solid with the analytical composition corresponding to **32** (Scheme 8). If, however, the reaction is

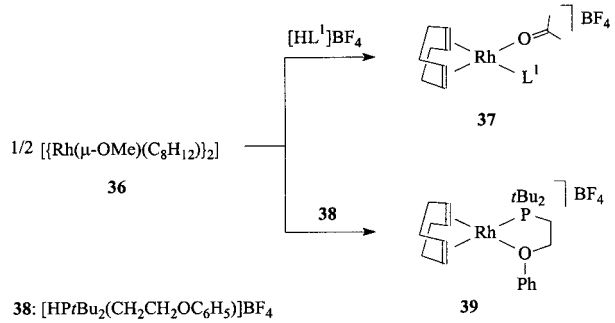



Scheme 8. $L^1 = \textit{i}Pr_2PCH_2CH_2C_6H_5$, $L^2 = \textit{t}Bu_2PCH_2CH_2C_6H_5$, S = acetone.

monitored by $^1H$ or $^{31}P$ NMR spectroscopy, the formation of an intermediate **31**, which also contains two hydrido ligands, can be observed. Typical features of **31** (which is stable under $H_2$ for hours but decomposes by replacing the hydrogen atmosphere for argon) are the high-field signal in the $^1H$ NMR spectrum at $\delta = -23.25$ and the doublet resonance in the $^{31}P$ NMR spectrum at $\delta = 94.4$. While the signal for the hydrido ligands appears as a doublet of doublets at 263 K, it is significantly broadened at room temperature, possibly due to an intramolecular rearrangement process. The halfsandwich-type compound **32** is soluble in nitromethane and dichloromethane, but is reconverted to the solvated species **31** in the presence of acetone. Attempts to isolate **31** by adding diethyl ether to the solution or by removal of the solvent led either to the formation of **32** or to decomposition. The dihydrido complex **32** (which can be stored under argon at $-20\,^\circ C$ for a few days) shows a characteristic signal for the Rh–H protons in the $^1H$ NMR spectrum at $\delta = -12.15$ and thus about 11 ppm downfield compared with that of **31**. Interestingly, whereas the ethene derivative **29**, which contains $L^1$ as the chelating ligand, also reacts with $H_2$ in acetone to give the solvato complex **30**, all attempts to isolate this compound or to transform it to the analogue of **32** failed.

A stepwise conversion of a $Rh(C_2H_4)$ to a $RhH_2$ species is also possible in the case of the nonchelating complexes **33** and **35** (Scheme 8). The reaction of **33** with $H_2$ in acetone is much faster than the reaction of **27** or **29** with hydrogen and affords in the initial step the tris(acetone) compound **34** in nearly quantitative yield. Since the light brown solid is thermally unstable and decomposes even under a hydrogen atmosphere, a correct elemental analysis could not be obtained. The $^1H$ NMR spectrum of **34** displays in $CD_2Cl_2$ a doublet of doublets at $\delta = -23.30$ for the hydrido ligands, the chemical shift being nearly identical to that of **31**. The solvato compound reacts in $CH_2Cl_2$ with excess benzene to give the halfsandwich-type complex **35**, which has been isolated as a light brown, moderately air-sensitive solid in 79% yield. Compared with **34**, the hydride resonance of **35** in the $^1H$ NMR spectrum is shifted by about 9 ppm to lower field, similarly as in the case of the chelate compound **32**. The signal for the protons of the coordinated benzene appears at $\delta = 6.99$ ppm and thus at somewhat higher field than for free $C_6H_6$.

**Cycloocta-1,5-dienerhodium(I) complexes with $L^1$ and $L^3$ as ligands**: The preparation of square-planar rhodium compounds with $L^1$ and $\textit{t}Bu_2PCH_2CH_2OC_6H_5$ ($L^3$) as ligands is possible by using the methoxy-bridged dimer **36** as the precursor. However, while treatment of **36** with the phosphonium salt $L^1 \cdot HBF_4$ in acetone affords the acetone-containing cation **37** (Scheme 9), the analogous reaction of **36** with




Scheme 9. $L^1 = \textit{i}Pr_2PCH_2CH_2C_6H_5$.

$[HP\textit{t}Bu_2(CH_2CH_2OC_6H_5)]BF_4$ (**38**) gives the chelate complex **39** in 78% yield. Compound **37** is isolated as an orange solid which is stable in acetone but decomposes slowly in dichloromethane. The IR spectrum of **37** displays a $\nu$(C=O) stretching mode at 1652 $cm^{-1}$ and thus at about the same position as for the iridium(I) counterpart.[26] In the $^1H$ NMR spectrum of **37** the signal for the protons of the coordinated acetone could not be observed which is probably due to a rapid ligand exchange between $(CH_3)_2C{=}O$ and $(CD_3)_2C{=}O$ used as the solvent.

The chelate complex **39** is a yellow air-stable solid that decomposes at 176 °C and is soluble in acetone and dichloromethane without decomposition. It is an analogue of the methoxy-functionalized phosphanerhodium(I) compounds $[Rh(C_8H_{12})(MeOCH_2CH_2PR_2\text{-}\kappa O,P)]X$ (R = Ph, *i*Pr, *t*Bu, Cy; X = $BPh_4$, $SbF_6$) which were prepared by Lindner et al. from the chloro-bridged dimer $[\{Rh(\mu\text{-}Cl)(C_8H_{12})\}_2]$ as the precursor.[27] The molecular structure of **39** is shown in Figure 5. The coordination geometry around the metal center corresponds to a distorted square with the oxygen atom, the phosphorus atom and the midpoints of the C=C double bonds

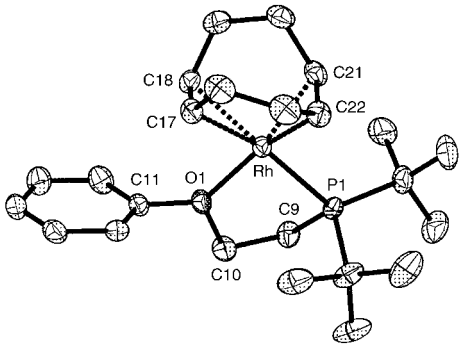



Figure 5. Molecular structure of **39**. Principal bond lengths [Å] and angles [°] (with estimated standard deviations in parentheses): Rh–O1 2.1750(12), Rh–P1 2.3255(4), Rh–C17 2.2423(16), Rh–C18 2.2102(16), Rh–C21 2.1122(17), Rh–C22 2.1106(17), C17–C18 1.366(3), C21–C22 1.404(3); O1-Rh-P1 81.59(3), Rh-P1-C9 98.51(5), Rh-O1-C10 121.50(10), Rh-O1-C11 124.29(9), P1-C9-C10 113.05(12), O1-C10-C9 107.99(13).

at the edges of the plane. The distances Rh–C17 and Rh–C18 are 0.10–0.13 Å longer than the distances Rh–C21 and Rh–C22, which is probably a consequence of the stronger *trans* influence of phosphorus compared with oxygen. The different donor properties of P and O may also explain why the bond C17–C18 is about 0.035 Å shorter than the C21–C22 bond. The five-membered chelate ring is not planar but possesses an envelope conformation with the carbon atom C2 bent out of the plane. The dihedral angle between the two planes O-Rh-P-C9 and O-C10-C9 is about 20°. The plane of the phenyl ring is nearly perpendicular to the basal plane of the envelope.

## Conclusion

The work presented herein illustrates that the functionalized phosphanes of the general composition $C_6H_5X(CH_2)_nPR_2$ with two bulky substituents at the phosphorus atom coordinate not only to rhodium(I) but also to rhodium(III) both as two-electron and (6 + 2)-electron donor ligands. However, the more noteworthy fact is that the bonding capabilities of the phosphanes used in these studies go beyond the L$^n$-$\kappa P$ and $\eta^6$-L$^n$-$\kappa P$ coordination modes. As it has been shown by the generation of the five-coordinate rhodium(III) complex **4c** and the isolation of its counterpart **17**, the interaction of the phosphanes L$^1$ and L$^2$ with the metal center can lead to an insertion of the metal into one of the C–H bonds of the phenyl group of the phosphane to give a new six-membered chelate ring system. This orthometalation reaction appears to be not only an energetically favored process but it is also reversible which is convincingly shown by the formation of **5**, **6**, **9**, **10** or **19**, **20**, **22**, **23**, **24** from **4a–c** or **17** and, in particular, by some labeling experiments. It appears that the formation of the carbonyl-, ethene-, and vinylidenerhodium(I) and the corresponding hydridorhodium(III) complexes from the mixture of **4a–c** and from **17** always proceed via the 14-electron intermediate [RhCl(L$^n$-$\kappa P$)$_2$] with the C–H activated compound representing the resting state. This assumption could be important for catalytic reactions carried out, for example, with the hydrido complexes **20**, **24**, **32**, and **35** as catalysts but this has to be proven by further investigations.

## Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by known procedures and distilled before used. The starting materials **2**,[28] **7**,[29] **26**,[7] **29**,[7] **33**, [7] **36**,[30] the phosphanes L$^1$ and L$^2$,[7] and the phosphonium salts L$^1\cdot$HBF$_4$ and **38**[26] were prepared as described in the literature. NMR spectra were recorded (at room temperature or at the temperature mentioned in the appropriate procedure) on Bruker AC 200 and AMX 400 instruments (abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; br, broadened signal; virt., virtual coupled), IR spectra on a Bruker IFS 25 FT-IR spectrometer, and mass spectra on a Finnigan MAT 90 instrument. Melting and decomposition points were determined by DTA. The molar conductivity $\Lambda$ was measured in nitromethane with a Schott Kondukto-meter CG 851.

**[Rh($\mu$-Cl)($C_8H_{14}$)($C_6H_5CH_2CH_2P$*i*$Pr_2$-$\kappa P$)]$_2$ (3)**: A suspension of **2** (941 mg, 1.31 mmol) in benzene (10 mL) was treated with a solution of L$^1$ (583 mg, 2.62 mmol) in pentane (5 mL) at room temperature. After the reaction mixture was stirred for 3 min, a red solution was formed which was filtered. The filtrate was brought to dryness in vacuo. A yellow solid was obtained, which was washed with pentane (4 × 10 mL each) and dried; yield 966 mg (78%); m.p. 30 °C (decomp); $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 7.17–7.05 (m, 10H; $C_6H_5$), 3.21 (m, 4H; =CH of $C_8H_{14}$), 2.81 (m, 4H; $PCH_2CH_2$), 2.57 (m, 8H; $PCH_2$ and $CH_2$ of $C_8H_{14}$), 1.94 (m, 4H; $PCHCH_3$), 1.75–1.34 (m, 20H; $CH_2$ of $C_8H_{14}$), 1.40 (dd, $J$(P,H) = 14.7, $J$(H,H) = 7.0 Hz, 12H; $PCHCH_3$), 1.06 ppm (dd, $J$(P,H) = 12.9, $J$(H,H) = 7.1 Hz, 12H; $PCHCH_3$); $^{13}$C NMR (100.6 MHz, $C_6D_6$): $\delta$ = 143.2 (d, $J$(P,C) = 11.4 Hz; *ipso*-C of $C_6H_5$), 128.9, 128.1, 126.5 (all s; $C_6H_5$), 61.1 (d, $J$(Rh,C) = 15.3 Hz; =CH of $C_8H_{14}$), 32.4 (s; $PCH_2CH_2$), 30.9, 30.7, 27.0 (all s; $CH_2$ of $C_8H_{14}$), 24.5 (d, $J$(P,C) = 25.8 Hz; $PCHCH_3$), 20.5 (d, $J$(P,C) = 20.0 Hz; $PCH_2$), 20.4, 18.7 ppm (both s; $PCHCH_3$); $^{31}$P NMR (162.0 MHz, $C_6D_6$): $\delta$ = 53.5 (d, $J$(Rh,P) = 184.8 Hz); elemental analysis (%) for $C_{44}H_{74}P_2Cl_2Rh_2$ (941.7): calcd: C 56.12, H 7.92; found: C 55.61, H 7.42.

**[Rh($\mu$-Cl)($C_6H_5CH_2CH_2P$*i*$Pr_2$-$\kappa P$)$_2$] (4a) and [Rh(H)Cl($C_6H_4CH_2$-$CH_2P$*i*$Pr_2$-$\kappa^2C,P$)($C_6H_5CH_2CH_2P$*i*$Pr_2$-$\kappa P$)] (4c)**: A suspension of **2** (130 mg, 0.18 mmol) in pentane (5 mL) was treated with a solution of L$^1$ (161 mg, 0.72 mmol) in pentane (3 mL), and the reaction mixture was stirred for 5 min at room temperature. A red solution was formed which was filtered. After the solvent was evaporated in vacuo, a red oily residue was obtained, which owing to the NMR spectra contained a mixture of mainly **4a** (ca. 80%) and **4c** (ca. 20%). The oily residue was dissolved in pentane (3 mL), and the solution was stored for 12 h at −60 °C. A red microcrystalline solid precipitated which was washed with small amounts of pentane (0 °C) and dried. It was identified as **4a**; yield 142 mg (67%), m.p. 40 °C (decomp); $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ = 7.33–6.86 (m, 20H; $C_6H_5$), 3.01 (m, 8H; $PCH_2CH_2$), 2.25–2.00 (m, 16H; $PCH_2$ and $PCHCH_3$), 1.56 (d virt. t, $N$ = 14.0, $J$(H,H) = 6.7 Hz, 24H; $PCHCH_3$), 1.21 ppm (d virt. t, $N$ = 11.9, $J$(H,H) = 7.0 Hz, 24H; $PCHCH_3$); $^{31}$P NMR (81.0 MHz, $C_6D_6$): $\delta$ = 51.2 ppm (d, $J$(Rh,P) = 198.4 Hz); elemental analysis (%) for $C_{56}H_{92}P_4Cl_2Rh_2$ (1166.0): calcd: C 57.69, H 7.95; found: C 57.96, H 8.11.

If the red solid was dissolved in [D$_6$]benzene and the solution stored for 1 h, an equilibrium mixture consisting of **4a** and **4c** was formed. Typical data for **4c**: $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ = −19.89 ppm (ddd, $J$(Rh,H) = 27.6, $J$(P,H) = 14.5 and 11.6 Hz, 1H; RhH); $^{31}$P NMR (81.0 MHz, $C_6D_6$): $\delta$ = 48.9 (dd, $J$(P,P) = 396.4, $J$(Rh,P) = 117.0 Hz; $P_A$), 26.9 ppm (dd, $J$(P,P) = 396.4, $J$(Rh,P) = 109.4 Hz; $P_B$); $P_A$ is the phosphorus atom of the chelating ligand and $P_B$ that of the monodentate ligand.

***trans*-[RhCl(CO)($C_6H_5CH_2CH_2P$*i*$Pr_2$-$\kappa P$)$_2$] (5)**: A suspension of **2** (105 mg, 0.15 mmol) in pentane (6 mL) was treated with L$^1$ (130 mg (0.59 mmol) and stirred for 5 min at room temperature. A red solution was formed, which was brought to dryness in vacuo. The oily residue was dissolved in pentane (4 mL) and the solution stirred under a CO atmosphere. A change of color from red to light yellow occured. After the solution was concentrated to about 2 mL in vacuo, a light yellow solid precipitated. The precipitate was filtered, washed with pentane (2 × 3 mL, −20 °C) and dried; yield 158 mg (86%); m.p. 57 °C; IR (KBr): $\tilde{\nu}$ = 1942 cm$^{-1}$ (CO); $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 7.35 (m, 4H; *ortho*-H of $C_6H_5$), 7.17 (m, 4H; *meta*-H of $C_6H_5$), 7.07 (m, 2H; *para*-H of $C_6H_5$), 3.14 (m, 4H; $PCH_2CH_2$) 2.21 (m, 4H; $PCH_2$), 2.17 (m, 4H; $PCHCH_3$), 1.30 (d virt. t, $N$ = 15.2, $J$(H,H) = 7.2 Hz, 12H; $PCHCH_3$), 1.13 ppm (d virt. t, $N$ = 14.0, $J$(H,H) = 7.0 Hz, 12H; $PCHCH_3$);

$^{13}$C NMR (100.6 MHz, $C_6D_6$): $\delta = 189.1$ (dt, $J$(Rh,C) = 73.4, $J$(P,C) = 15.8 Hz; CO), 143.5 (virt. t, $N = 13.4$ Hz; *ipso*-C of $C_6H_5$), 128.8, 128.6, 126.4 (all s; $C_6H_5$), 33.1 (s; $PCH_2CH_2$), 25.6 (virt. t, $N = 23.4$ Hz; $PCHCH_3$), 25.5 (virt. t, $N = 20.3$ Hz; $PCH_2$), 20.1, 18.7 ppm (both s; $PCHCH_3$); $^{31}$P NMR (162.0 MHz, $C_6D_6$): $\delta = 41.2$ ppm (d, $J$(Rh,P) = 118.7 Hz); elemental analysis (%) for $C_{29}H_{46}OP_2ClRh$ (611.0): calcd: C 57.01, H 7.59; found: C 56.63, H 7.48.

***trans*-[RhCl($C_2H_4$)($C_6H_5CH_2CH_2P$*i*$Pr_2$-κP)$_2$] (6)**: Method A: A suspension of **2** (111 mg, 0.15 mmol) in pentane (6 mL) was treated with L$^1$ (138 mg, 0.62 mmol) and stirred for 5 min at room temperature. After the solvent was evaporated in vacuo, the red oily residue was dissolved in pentane (3 mL) and the solution was stirred under an ethene atmosphere. A gradual change of color from red to orange-red occurred and after about 5 min a yellow solid precipitated. After the reaction mixture was continuously stirred for 15 min, the solid was separated from the mother liquor, washed with pentane (3 × 3 mL, 0 °C) and dried; yield 143 mg (78 %).

Method B: A suspension of **7** (89 mg, 0.23 mmol) in acetone (4 mL) was treated with a solution of L$^1$ (203 mg, 0.92 mmol) in acetone (3 mL) at room temperature. A yellow solution was formed, from which the solvent was evaporated in vacuo. The remaining yellow solid was washed with pentane (3 × 4 mL, 0 °C) and dried; yield 210 mg (75 %); m.p. 46 °C (decomp); $^1$H NMR (400 MHz, $C_6D_6$): $\delta = 7.20 - 7.14$ (m, 8H; *ortho*- and *meta*-H of $C_6H_5$), 7.07 (m, 2H; *para*-H of $C_6H_5$), 2.85 (m, 4H; $PCH_2CH_2$), 2.61 (m, 4H; $C_2H_4$), 2.39 (m, 4H; $PCHCH_3$), 1.76 (m, 4H; $PCH_2$), 1.38 (d virt. t, $N = 14.1$, $J$(H,H) = 7.2 Hz, 12H; $PCHCH_3$), 1.14 ppm (d virt. t, $N$ = 13.1, $J$(H,H) = 7.2 Hz, 12H; $PCHCH_3$); $^{13}$C NMR (100.6 MHz, $C_6D_6$): $\delta$ = 143.5 (virt. t, $N = 11.2$ Hz; *ipso*-C of $C_6H_5$), 128.9, 128.3, 126.4 (all s; $C_6H_5$), 38.1 (br d, $J$(Rh,C) = 15.3 Hz; $C_2H_4$), 32.3 (s; $PCH_2CH_2$), 23.2 (virt. t, $N$ = 20.3 Hz; $PCHCH_3$), 20.3, 19.3 (both s; $PCHCH_3$), 19.9 ppm (virt. t, $N$ = 13.2 Hz; $PCH_2$); $^{31}$P NMR (162.0 MHz, $C_6D_6$): $\delta = 27.5$ ppm (d, $J$(Rh,P) = 120.4 Hz); elemental analysis (%) for $C_{30}H_{50}P_2ClRh$ (611.0): calcd: C 58.97, H 8.25; found: C 58.66; H 7.79.

**[$RhH_2Cl(C_6H_5CH_2CH_2P$*i*$Pr_2$-κP)$_2$] (8)**: A suspension of **6** (136 mg, 0.22 mmol) in pentane (5 mL) was stirred for about 10 s under a hydrogen atmosphere. A light yellow solution was formed, which was brought to dryness in vacuo. The NMR spectra of the orange oily residue revealed that compound **8** was obtained as the dominating species (ca. 90 %) together with some by-products. Attempts to separate the by-products by repeated recrystallization or chromatographic techniques failed. Continuous stirring of the mixture in pentane under $H_2$ did also not lead to complete conversion to **8**. Spectroscopic data for **8**: $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ = 7.37 – 7.05 (m, 10H; $C_6H_5$), 3.10 (m, 4H; $PCH_2CH_2$), 2.10 (m, 8H; $PCH_2$ and $PCHCH_3$), 1.18 (d virt. t, $N = 14.8$, $J$(H,H) = 6.9 Hz, 12H; $PCHCH_3$), 1.12 (d virt. t, $N = 13.8$, $J$(H,H) = 6.9 Hz, 12H; $PCHCH_3$), −21.62 ppm (dt, $J$(Rh,H) = 25.6, $J$(P,H) = 14.8 Hz, 2H; RhH); $^{13}$C NMR (50.3 MHz, $C_6D_6$): $\delta = 143.7$ (virt. t, $N = 13.6$ Hz; *ipso*-C of $C_6H_5$), 128.8, 128.3, 126.3 (all s; $C_6H_5$), 33.4 (s; $PCH_2CH_2$), 26.8 (virt. t, $N = 20.1$ Hz, $PCH_2$), 25.3 (virt. t, $N = 23.7$ Hz; $PCHCH_3$), 19.8, 19.5 ppm (both s; $PCHCH_3$); $^{31}$P NMR (81.0 MHz, $C_6D_6$): $\delta = 52.1$ ppm (d, $J$(Rh,P) = 111.9 Hz).

***trans*-[RhCl(=C=CHPh)($C_6H_5CH_2CH_2P$*i*$Pr_2$-κP)$_2$] (9)**: A suspension of **2** (145 mg, 0.20 mmol) in pentane (9 mL) was treated with L$^1$ (180 mg, 0.81 mmol) and stirred for 5 min at room temperature. The solvent was evaporated in vacuo, the oily residue was dissolved in toluene (5 mL) and the solution cooled to −78 °C. After phenylacetylene (44 μL, 0.40 mmol) was added, the solution was warmed to room temperature and then stirred for 8 h. A stepwise change of color from yellow to red-brown and finally to blue-violet occurred. The volatile substances were removed in vacuo, the residue was dissolved in hexane (1 mL) and the solution chromatographed on $Al_2O_3$ (neutral, activity grade III). With hexane, an off-white fraction was eluted which was thrown away. With benzene, a blue fraction was eluted which was brought to dryness in vacuo. The oily residue was dissolved in pentane (2 mL) and the solution was stored at −60 °C. A blue-violet solid precipitated, which was filtered, washed with pentane (2 × 1 mL, 0 °C) and dried; yield 191 mg (69 %); m.p. 66 °C (decomp); IR (pentane): $\delta = 1647$, 1625, 1599 cm$^{-1}$ (C=C); $^1$H NMR (400 MHz, $C_6D_6$): $\delta = 7.25 - 7.04$ (m, 14H; $C_6H_5$), 6.87 (m, 1H; *para*-H of $=CHC_6H_5$), 3.11 (m, 4H; $PCH_2CH_2$), 2.41 (m, 4H; $PCHCH_3$), 2.33 (m, 4H; $PCH_2$), 1.66 (t, $J$(P,H) = 3.2 Hz, 1H; Rh = C = CH), 1.35 (d virt. t, $N = 15.0$, $J$(H,H) = 7.3 Hz, 12H; $PCHCH_3$), 1.17 ppm (d virt. t, $N = 13.5$, $J$(H,H) = 7.0 Hz, 12H; $PCHCH_3$); $^{13}$C NMR (100.6 MHz, $C_6D_6$): $\delta = 296.5$ (dt, $J$(Rh,C) = 58.5, $J$(P,C) = 16.5 Hz; Rh=*C*=CH), 143.4 (virt. t, $N = 14.0$ Hz; *ipso*-C of $CH_2C_6H_5$), 128.8, 128.7, 128.5 (all s; $CH_2C_6H_5$), 126.3, 125.5, 125.3 (all s; $=CHC_6H_5$), 125.4 (t, $J$(P,C) = 2.5 Hz; *ipso*-C of $=CHC_6H_5$), 112.2 (dt, $J$(Rh,C) = 15.3, $J$(P,C) = 6.4 Hz; Rh=C=*C*H), 32.7 (s; $PCH_2CH_2$), 24.4 (virt. t, $N = 22.9$ Hz; $PCHCH_3$), 23.8 (virt. t, $N = 19.1$ Hz; $PCH_2$), 20.6 (virt. t, $N = 2.5$ Hz; $PCHCH_3$), 19.0 ppm (s; $PCHCH_3$); $^{31}$P NMR (162.0 MHz, $C_6D_6$): $\delta = 35.1$ ppm (d, $J$(Rh,P) = 133.9 Hz); elemental analysis (%) for $C_{36}H_{52}P_2ClRh$ (685.1): calcd: C 63.11, H 7.65; found: C 62.58, H 7.23.

***trans*-[RhCl{=C=CHC(OH)Ph$_2$}($C_6H_5CH_2CH_2P$*i*$Pr_2$-κP)$_2$] (10)**: A suspension of **2** (735 mg, 1.03 mmol) in pentane (20 mL) was treated with L$^1$ (911 mg, 4.10 mmol) and stirred for 5 min at room temperature. The solvent was evaporated in vacuo, the oily residue was dissolved in toluene (8 mL) and the solution cooled to −78 °C. After a solution of HC≡CC(OH)Ph$_2$ (427 mg, 2.05 mmol) in toluene (4 mL) was added, the reaction mixture was slowly warmed to room temperature and stirred for 12 h. A gradual change of color from red to brown occurred. The volatile substances were removed in vacuo and the oily residue extracted twice with pentane (20 mL each). After the combined extracts were concentrated in vacuo to about 1 mL, a green solid precipitated. The precipitate was separated from the mother liquor, washed with pentane (5 × 5 mL, 0 °C) and dried; yield 1.21 g (75 %); m.p. 97 °C (decomp); IR (benzene): $\tilde{\nu} = 3567$ (OH), 1648 cm$^{-1}$ (C=C); $^1$H NMR (200 MHz, $C_6D_6$): $\delta = 7.41 - 7.37$ (m, 4H; $C_6H_5$), 7.30 – 6.92 (m, 16H; $C_6H_5$), 3.10 (m, 4H; $PCH_2CH_2$), 2.84 (s, 1H; OH), 2.41 – 2.23 (m, 8H; $PCH_2$ and $PCHCH_3$), 1.40 (dt, $J$(P,H) = 3.3, $J$(Rh,H) = 0.7 Hz, 1H; Rh=C=CH), 1.26 (d virt. t, $N = 14.6$, $J$(H,H) = 7.3 Hz, 12H; $PCHCH_3$), 1.14 ppm (d virt. t, $N = 13.5$, $J$(H,H) = 6.9 Hz, 12H; $PCHCH_3$); $^{13}$C NMR (50.3 MHz, $C_6D_6$): $\delta = 286.4$ (dt, $J$(Rh,C) = 60.1, $J$(P,C) = 16.2 Hz; Rh=C=CH), 149.3 (s; *ipso*-C of $C(OH)(C_6H_5)_2$), 143.5 (virt. t, $N = 13.4$ Hz; *ipso*-C of $CH_2C_6H_5$), 128.9, 128.7, 128.3, 127.1, 126.4, 125.9 (all s; $C_6H_5$), 118.6 (dt, $J$(Rh,C) = 15.3, $J$(P,C) = 6.7 Hz; Rh=C=*C*H), 67.9 (s; $C(OH)(C_6H_5)_2$), 32.8 (s; $PCH_2CH_2$), 24.4 (virt. t, $N = 22.9$ Hz; $PCHCH_3$), 23.4 (virt. t, $N = 19.1$ Hz; $PCH_2$), 20.5, 19.0 ppm (both s, $PCHCH_3$); $^{31}$P NMR (81.0 MHz, $C_6D_6$): $\delta = 35.0$ ppm (d, $J$(Rh,P) = 132.2 Hz); elemental analysis (%) for $C_{43}H_{58}OP_2ClRh$ (791.2): calcd: C 65.27, H 7.39; found: C 64.97, H 7.05.

***trans*-[RhCl(=C=C=CPh$_2$)($C_6H_5CH_2CH_2P$*i*$Pr_2$-κP)$_2$] (11)**: The first part of the procedure is analogous to that described for **10**. From **2** (518 mg, 0.72 mmol), L$^1$ (642 mg, 2.89 mmol) and HC≡CC(OH)Ph$_2$ (301 mg, 1.44 mmol) the precursor **10** was generated in situ. After removal of the solvent, the oily residue was dissolved in benzene (3 mL) and the solution was layed on a column filled with $Al_2O_3$ (acidic, activity grade III, height of column 15 cm). A smooth change of color from green to orange-red occurred. After 72 h the orange-red fraction was eluted with benzene and the eluate was brought to dryness in avcuo. The oily residue was washed with pentane (3 × 10 mL, 0 °C) to give an orange solid; yield 926 mg (83 %); m.p. 97 °C(decomp); IR (benzene): $\tilde{\nu} = 1963$, 1879 cm$^{-1}$ (C=C=C); $^1$H NMR (300 MHz, $C_6D_6$): $\delta = 7.88$ (m, 4H; *ortho*-H of $=C(C_6H_5)_2$), 7.46 (m, 2H; *para*-H of $=C(C_6H_5)_2$), 7.27 – 6.97 (m, 10H; $CH_2C_6H_5$), 6.76 (m, 4H; *meta*-H of $=C(C_6H_5)_2$), 3.15 (m, 4H; $PCH_2CH_2$), 2.56 (m, 4H; $PCH_2$), 2.47 (m, 4H; $PCHCH_3$), 1.33 (d virt. t, $N = 14.9$, $J$(H,H) = 7.4 Hz, 12H; $PCHCH_3$), 1.25 ppm (d virt. t, $N = 13.9$, $J$(H,H) = 6.9 Hz, 12H; $PCHCH_3$); $^{13}$C NMR (75.5 MHz, $C_6D_6$): $\delta = 245.6$ (dt, $J$(Rh,C) = 15.3, $J$(P,C) = 7.3 Hz; Rh=C=*C*=C), 223.3 (dt, $J$(Rh,C) = 64.3, $J$(P,C) = 8.0 Hz; Rh=*C*=C=C), 154.3 (t, $J$(P,C) = 2.6 Hz; Rh=C=C=*C*), 143.9 (virt. t, $N = 13.4$ Hz; *ipso*-C of $CH_2C_6H_5$), 142.5 (br s; *ipso*-C of $=C(C_6H_5)_2$), 130.0, 128.6, 128.5, 127.2, 126.0, 123.9 (all s; $C_6H_5$), 33.2 (s; $PCH_2CH_2$), 24.7 (virt. t, $N = 21.7$ Hz; $PCHCH_3$), 24.1 (virt. t, $N = 18.0$ Hz; $PCH_2$), 20.8 (virt. t, $N = 4.6$ Hz; $PCHCH_3$), 18.9 ppm (s; $PCHCH_3$); $^{31}$P NMR (81.0 MHz, $C_6D_6$): $\delta = 31.1$ (d, $J$(Rh,P) = 129.7 Hz); elemental analysis (%) for $C_{43}H_{56}P_2ClRh$ (773.2): calcd: C 66.80, H 7.30; found: C 66.51, H 7.35.

***trans*-[RhCl(OH)(=C=C=CPh$_2$)($C_6H_5CH_2CH_2P$*i*$Pr_2$-κP)$_2$] (12)**: A solution of **11** (615 mg, 0.80 mmol) in a mixture of benzene (7 mL) and *tert*-$C_4H_9OH$ (5 mL) was treated with KO*t*Bu (179 mg, 1.60 mmol) and stirred for 2 h at room temperature. A gradual change of color from orange-red to brown occurred.The solvent was evaporated in vacuo, and the residue was extracted with pentane (25 mL). After the extract was brought to dryness in vacuo, a brown solid was obtained which was washed with pentane (2 × 4 mL, 0 °C) and dried; yield 353 mg (59 %); m.p. 28 °C (decomp); IR ($C_6H_6$): $\tilde{\nu} = 3642$ (OH), 1859 cm$^{-1}$ (C=C=C); $^1$H NMR (200 MHz, $C_6D_6$): $\delta = 7.96$ (m, 4H; *ortho*-H of $=C(C_6H_5)_2$), 7.47 (m, 2H; *para*-H of $=C(C_6H_5)_2$], 7.24 – 7.01 (m, 10H; $CH_2C_6H_5$), 6.80 (m, 4H; *meta*-H of $=C(C_6H_5)_2$), 3.15 (m, 4H; $PCH_2CH_2$), 2.49 – 2.25 (m, 8H; $PCH_2$ and

PC*H*CH$_3$), 1.57 (t, $J$(P,H) = 5.5 Hz, 1H; OH), 1.33 (d virt. t, $N$ = 15.0, $J$(H,H) = 7.3 Hz, 12H; PCHC$H_3$), 1.24 ppm (d virt. t, $N$ = 13.2, $J$(H,H) = 6.6 Hz, 12H; PCHC$H_3$); $^{13}$C NMR (50.3 MHz, $C_6D_6$): $\delta$ = 245.2 (dt, $J$(Rh,C) = 12.7, $J$(P,C) = 6.4 Hz; Rh=C=*C*=C), 221.5 (dt, $J$(Rh,C) = 50.9, $J$(P,C) = 19.1 Hz; Rh=*C*=C=C), 154.4 (s; Rh=C=C=*C*), 154.3 (s; *ipso*-C of =C($C_6H_5$)$_2$), 144.0 (virt. t, $N$ = 12.7 Hz; *ipso*-C of CH$_2$$C_6H_5$), 129.8, 128.7, 128.6, 126.2, 126.0, 123.8 (all s; $C_6H_5$), 33.4 (s; PCH$_2$$CH_2$), 24.0 (virt. t, $N$ = 21.6 Hz; P*C*HCH$_3$), 22.8 (virt. t, $N$ = 15.3 Hz; PCH$_2$), 20.6, 18.6 ppm (both s; PCH*C*H$_3$); $^{31}$P NMR (81.0 MHz, $C_6D_6$): $\delta$ = 34.1 ppm (d, $J$(Rh,P) = 145.0 Hz); elemental analysis (%) for $C_{43}H_{57}OP_2Rh$ (754.8): calcd: C 68.43, H 7.61; found: C 67.77, H 7.30.

**Preparation of *trans*-[Rh(O=CMe$_2$)(=C=C=CPh$_2$)($C_6H_5CH_2CH_2P$*i*Pr$_2$-$\kappa$P)$_2$]PF$_6$ (14) via *trans*-[Rh(OH$_2$)(=C=C=CPh$_2$)($C_6H_5CH_2CH_2P$*i*Pr$_2$-$\kappa$P)$_2$]PF$_6$ (13)**: A solution of **12** (129 mg, 0.17 mmol) in acetone (3 mL) was treated at $-78\,^{\circ}$C with $NH_4PF_6$ (28 mg, 0.17 mmol). A rapid change of color from light brown to red occurred. After the reaction mixture was smoothly warmed to room temperature, the $^1$H NMR spectrum revealed that compound **13** was formed. While attempts to isolate **13** failed, the compound slowly allowed to react (8 h) in acetone to give **14**. The solution was brought to dryness in vacuo, and the red oily residue was washed twice with diethyl ether and pentane (5 mL each, 0 °C). A red solid of composition **14** was obtained and dried; yield 114 mg (71%); m.p. 34 °C(decomp); $\Lambda_M$ = 102.7 cm$^2\,\Omega^{-1}$mol$^{-1}$; IR (CH$_2$Cl$_2$): $\delta$ = 1924 cm$^{-1}$ (C=C=C); $^1$H NMR (400 MHz, [D$_6$]acetone): $\delta$ = 7.88 (m, 4H, *ortho*-H of =C($C_6H_5$)$_2$], 7.31–7.12 (m, 16H; $C_6H_5$), 3.01 (m, 4H; PCH$_2$$CH_2$), 2.48 (m, 4H; PC*H*CH$_3$), 2.29 (m, 4H; PCH$_2$), 1.30 (d virt. t, $N$ = 14.2, $J$(H,H) = 7.2 Hz, 24H; PCHC$H_3$); $^{13}$C NMR (100.6 MHz, [D$_6$]acetone): $\delta$ = 257.7 (dt, $J$(Rh,C) = 55.6, $J$(P,C) = 19.1 Hz; Rh=*C*=C=C), 227.7 (dt, $J$(Rh,C) = 15.3, $J$(P,C) = 6.0 Hz; Rh=C=*C*=C), 151.7 (s; Rh=C=C=*C*), 150.9 (s; *ipso*-C of =C($C_6H_5$)$_2$), 143.0 (virt. t, $N$ = 13.1 Hz, *ipso*-C of CH$_2$$C_6H_5$), 130.8, 130.4, 129.3, 128.5, 126.9, 126.7 (all s; $C_6H_5$), 32.3 (s; PCH$_2$$CH_2$), 25.5 (virt. t, $N$ = 22.9 Hz; P*C*HCH$_3$), 24.5 (virt. t, $N$ = 18.5 Hz; PCH$_2$), 20.1, 19.4 ppm (both s; PCH*C*H$_3$); $^{31}$P NMR (162.0 MHz, [D$_6$]acetone): $\delta$ = 30.7 (d, $J$(Rh,P) = 133.0 Hz; *i*Pr$_2$P), −144.1 ppm (sept, $J$(F,P) = 708.5 Hz; PF$_6$); elemental analysis (%) for $C_{46}H_{62}OF_6P_3Rh$ (940.8): calcd: C 58.73, H 6.64; found: C 58.77; H 6.48.

Data for **13**: $^1$H NMR (200 MHz, [D$_6$]acetone): $\delta$ = 7.86 (m, 4H; *ortho*-H of =C($C_6H_5$)$_2$], 7.31–7.08 (m, 16H; $C_6H_5$), 2.99 (m, 4H; PCH$_2$$CH_2$), 2.56 (m, 4H; PC*H*CH$_3$), 2.41 (m, 4H; PCH$_2$), 1.35 (d virt. t, $N$ = 13.4, $J$(H,H) = 6.7 Hz, 12H; PCHC$H_3$), 1.31 ppm (d virt. t, $N$ = 14.0, $J$(H,H) = 7.3 Hz, 12H; PCHC$H_3$); $^{31}$P NMR (81.0 MHz, [D$_6$]acetone): $\delta$ = 33.7 (d, $J$(Rh,P) = 132.3 Hz; *i*Pr$_2$P), −142.7 ppm (sept, $J$(F,P) = 707.0 Hz; PF$_6$).

**[Rh($\mu$-Cl)($C_8H_{14}$)($C_6H_5CH_2CH_2P$*t*Bu$_2$-$\kappa$P)]$_2$ (15)**: A suspension of **2** (716 mg, 1.00 mmol) in benzene (10 mL) was treated with a solution of L$^2$ (500 mg, 2.00 mmol) in pentane (5 mL) and stirred for 3 min at room temperature. An orange-red solution resulted which was filtered. After the solvent was evaporated in vacuo, a yellow solid was obtained which was washed with pentane (5 × 6 mL, 0 °C) and dried; yield 729 mg (73%); m.p. 70 °C (decomp);$^1$H NMR (200 MHz, $C_6D_6$): $\delta$ = 7.18–6.98 (m, 10H; $C_6H_5$), 3.65 (m, 4H; =CH of $C_8H_{14}$), 2.93 (m, 4H; PCH$_2$$CH_2$), 2.53, 2.05 (both m, 4 H each; CH$_2$ of $C_8H_{14}$), 1.81–1.33 (m, 20H; PCH$_2$ and CH$_2$ of $C_8H_{14}$), 1.43 ppm (d, $J$(P,H) = 12.4 Hz, 36H; PCCH$_3$); $^{13}$C NMR (50.3 MHz, $C_6D_6$): $\delta$ = 143.4 (d, $J$(P,C) = 10.4 Hz; *ipso*-C of $C_6H_5$), 130.3, 129.0, 126.6 (all s; $C_6H_5$), 59.6 (d, $J$(Rh,C) = 16.2 Hz; =CH of $C_8H_{14}$), 36.9 (d, $J$(P,C) = 16.9 Hz; P*C*CH$_3$), 33.2 (s; PCH$_2$$CH_2$), 31.3 (d, $J$(P,C) = 3.2 Hz; PC*C*H$_3$) 30.9, 30.8, 27.2 (all s; CH$_2$ of $C_8H_{14}$), 21.9 ppm (d, $J$(P,C) = 13.0 Hz; PCH$_2$); $^{31}$P NMR (81.0 MHz, $C_6D_6$): $\delta$ = 63.3 ppm (d, $J$(Rh,P) = 190.7 Hz); elemental analyis (%) for $C_{48}H_{82}P_2Cl_2Rh_2$ (997.8): calcd: C 57.78, H 8.28, Rh 20.62; found: C 58.25, H 8.26, Rh 20.70.

**[Rh($\mu$-Cl)($C_2H_4$)($C_6H_5CH_2CH_2P$*t*Bu$_2$-$\kappa$P)]$_2$ (16)**: Method A: A suspension of **7** (73 mg, 0.19 mmol) in pentane (5 mL) was treated with a solution of L$^2$ (94 mg, 0.38 mmol) in pentane (2 mL) and stirred for 3 min at room temperature. A yellow solution resulted and a yellow solid began to precipitate. To complete the precipitation, the solution was concentrated to about 3 mL in vacuo and stored for 3 h. The yellow solid was filtered, washed with pentane (3 × 3 mL, 0 °C) and dried; yield 131 mg (83%).

Method B: A suspension of **7** (66 mg, 0.17 mmol) and **17** (217 mg, 0.34 mmol) in pentane (5 mL) was stirred for 3 min at room temperature. A yellow solution resulted which was worked up as described for method a; yield 122 (86%); m.p. 52 °C (decomp); $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ = 7.17–6.98 (m, 10H; $C_6H_5$), 3.56, 3.06 (both m, 4 H each; $C_2H_4$), 2.84 (m, 4H; PCH$_2$C$H_2$), 1.56 (m, 4H; PCH$_2$), 1.35 ppm (d, $J$(P,H) = 12.4 Hz, 36H; PCCH$_3$); $^{13}$C NMR (50.3 MHz, $C_6D_6$): $\delta$ = 143.1 (d, $J$(Rh,C) = 10.4 Hz; *ipso*-C of $C_6H_5$), 128.9, 128.3, 126.6 (all s; $C_6H_5$), 44.7 (d, $J$(Rh,C) = 14.9 Hz; $C_2H_4$), 36.8 (d, $J$(P,C) = 18.2 Hz; P*C*CH$_3$), 32.9 (s; PCH$_2$$CH_2$), 31.0 (d, $J$(P,C) = 3.3 Hz; PC*C*H$_3$), 22.4 ppm (d, $J$(P,C) = 15.6 Hz; PCH$_2$); $^{31}$P NMR (81.0 MHz, $C_6D_6$): $\delta$ = 65.8 ppm (d, $J$(Rh,P) = 185.7 Hz); elemental analysis (%) for $C_{36}H_{62}P_2Cl_2Rh_2$ (833.6): calcd: C 51.87, H 7.50; found: C 51.53, H 7.54.

**[RhHCl($C_6H_4CH_2CH_2P$*t*Bu$_2$-$\kappa^2C,P$)($C_6H_5CH_2CH_2P$*t*Bu$_2$-$\kappa$P)] (17)**: Method A: A suspension of **2** (1.51 g, 2.11 mmol) in pentane (10 mL) was treated with L$^2$ (2.11 g, 8.43 mmol) and stirred for 15 min at room temperature. A clean yellow solution resulted. The solvent was evaporated in vacuo, and the oily residue was layered with pentane (10 mL). After 8 h a yellow solid was obtained, which was separated from the mother liquor, washed with pentane (5 × 4 mL) and dried. The pentane washings were combined, then concentrated to about 3 mL in vacuo, and the solution was stirred for 3 h at room temperature. A yellow solid precipitated which was separated from the mother liquor, washed with pentane (5 × 3 mL each) and dried. This procedure was repeated three times; overall yield 2.29 g (85%).

Method B: Similar to method A, but using **7** (303 mg, 0.78 mmol) and L$^2$ (780 mg, 3.12 mmol) as starting materials; yield 808 mg (81%); m.p. 97 °C (decomp); IR (KBr): $\tilde{\nu}$ = 2170 cm$^{-1}$ (RhH); $^1$H NMR (600 MHz, $C_6D_6$): $\delta$ = 8.34 (m, 1H; $C_6H_4$), 7.37 (m, 2H; *ortho*-H of $C_6H_5$), 7.20 (m, 2H; *meta*-H of $C_6H_5$), 7.08 (m, 1H; para-H of $C_6H_5$), 6.80 (m, 2H; $C_6H_4$), 6.66 (m, 1H; $C_6H_4$), 3.74, 3.20 (both m, 1H each; C$H_2$$C_6H_2$), 2.77, 2.70 (both m; 1H each; C$H_2$$C_6H_2$), 2.27, 2.10 (both m, 1H each; C$H_2$CH$_2$$C_6H_5$), 1.41, 0.83 (both m, 1 H each; C$H_2$CH$_2$$C_6H_4$), 1.31 (d, $J$($P_A$,H) = 12.3 Hz, 9H; $P_A$CCH$_3$), 1.22 (d, $J$($P_B$,H) = 12.1 Hz, 9H; $P_B$CCH$_3$), 1.15 (d, $J$($P_A$,H) = 13.0 Hz, 9H; $P_A$CCH$_3$), 1.04 (d, $J$($P_B$,H) = 12.1 Hz, 9H; $P_B$CCH$_3$), −18.11 ppm (ddd, $J$(Rh,H) = 22.9, $J$($P_A$,H) = 9.5, $J$($P_B$,H) = 15.9 Hz, 1H; RhH); $^{13}$C NMR (150.9 MHz, $C_6D_6$): $\delta$ = 146.9 (ddd, $J$(Rh,C) = 34.2, $J$($P_A$,C) = 12.0, $J$($P_B$,C) = 5.8 Hz; RhC of $C_6H_4$), 144.4 (d, $J$($P_B$,C) = 12.6 Hz; *ipso*-C of $C_6H_5$), 144.3 (d, $J$($P_A$,C) = 8.6 Hz; *ipso*-C of $C_6H_4$), 136.6 (dd, $J$($P_B$,C) = 6.9, $J$(Rh,C) = 2.8 Hz; $C_6H_4$), 128.8, 128.7, 126.2 (all s; $C_6H_5$), 126.3, 123.4, 122.9 (all s; $C_6H_4$), 42.2 (dd, $J$(Rh,C) = 5.7, $J$($P_A$,C) = 5.2 Hz; C$H_2$$C_6H_4$), 37.5 (dd, $J$($P_A$,C) = 10.3, $J$($P_B$,C) = 6.9 Hz; $P_A$*C*CH$_3$), 37.0 (dd, $J$($P_A$,C) = 2.9, $J$($P_B$,C) = 11.5 Hz; $P_B$*C*CH$_3$), 36.1 (ddd, $J$($P_A$,C) = 2.3, $J$($P_B$,C) = 12.1, $J$(Rh,C) = 1.9 Hz; $P_B$*C*CH$_3$), 35.8 (d, $J$($P_A$,C) = 16.1 Hz; $P_A$*C*CH$_3$), 33.0 (s; *C*H$_2$$C_6H_5$), 31.0 (d, $J$($P_B$,C) = 4.0 Hz; $P_B$C*C*H$_3$), 30.4 (d, $J$($P_A$,C) = 2.9 Hz; $P_A$C*C*H$_3$), 30.3 (d, $J$($P_B$,C) = 3.4 Hz; $P_B$C*C*H$_3$), 29.5 (d, $J$($P_A$,C) = 1.9 Hz; $P_A$C*C*H$_3$), 25.7 (dd, $J$($P_B$,C) = 6.9, $J$($P_A$,C) = 2.3 Hz; *C*H$_2$CH$_2$$C_6H_5$), 19.1 ppm (d, $J$($P_A$,C) = 29.3 Hz; *C*H$_2$CH$_2$$C_6H_4$); $^{31}$P NMR (162.0 MHz, $C_6D_6$): $\delta$ = 65.7 (dd, $J$($P_A$,$P_B$) = 366.2, $J$(Rh,$P_A$) = 120.4 Hz; *t*Bu$_2$$P_A$), 43.0 ppm (dd, $J$($P_A$,$P_B$) = 366.2, $J$(Rh,$P_B$) = 110.2 Hz; *t*Bu$_2$$P_B$); $P_A$ is the phosphorus atom of the chelate ring and $P_B$ the phosphorus atom of the monodentate ligand; elemental analysis (%) for $C_{32}H_{54}P_2ClRh$ (639.1): calcd: C 60.14, H 8.52, Rh 16.10; found: C 59.70, H 8.35, Rh 16.58.

***trans*-[RhCl(CO)($C_6H_5CH_2CH_2P$*t*Bu$_2$-$\kappa$P)$_2$] (19)**: A suspension of **17** (97 mg, 0.15 mmol) in pentane (6 mL) was stirred under a CO atmosphere for 3 min at room temperature. A light yellow solution resulted from which a yellow solid began to precipitate. After the solution was stored for 2 h at 0 °C, the yellow solid was filtered, washed with pentane (2 × 5 mL) and dried; yield 93 mg (93%); m.p. 192 C (decomp); IR (KBr): $\tilde{\nu}$ = 1937 cm$^{-1}$ (CO); $^1$H NMR (400 MHz, [D$_8$]toluene, 343 K): $\delta$ = 7.44 (m, 4H; *ortho*-H of $C_6H_5$), 7.16 (m, 4H; *meta*-H of $C_6H_5$), 7.05 (m, 2H; *para*-H of $C_6H_5$), 3.20 (m, 4H; PCH$_2$C$H_2$) 2.49 (m, 4H; PCH$_2$), 1.42 ppm (virt. t, $N$ = 12.6 Hz, 36H; PCCH$_3$); $^{13}$C NMR (100.6 MHz, [D$_8$]toluene, 343 K): $\delta$ = 190.2 (dt, $J$(Rh,C) = 73.4, $J$(P,C) = 15.3 Hz; CO) 144.0 (virt. t, $N$ = 13.4 Hz; *ipso*-C of $C_6H_5$), 128.9, 128.8, 126.5 (all s; $C_6H_5$), 36.0 (virt. t, $N$ = 15.3 Hz; P*C*CH$_3$), 33.8 (s; PCH$_2$$CH_2$), 30.9 (virt. t, $N$ = 4.8 Hz; PC*C*H$_3$), 24.3 ppm (virt. t, $N$ = 15.2 Hz; PCH$_2$); $^{31}$P NMR (162.0 MHz, [D$_8$]toluene, 343 K): $\delta$ = 57.8 ppm (d, $J$(Rh,P) = 125.5 Hz); $^{31}$P NMR (162.0 MHz, $C_6D_6$, 293 K): $\delta$ = 54.2 ppm (br s); $^{31}$P NMR (162.0 MHz, [D$_8$]toluene, 223 K): $\delta$ = 58.9 (dd, $J$($P_A$,$P_B$) = 312.0, $J$(Rh,$P_A$) = 118.7 Hz; *t*Bu$_2$$P_A$ of rotamer R$^1$), 58.1 (d, $J$(Rh,P) = 120.4 Hz; *t*Bu$_2$P of rotamer R$^2$), 47.4 (dd, $J$($P_A$,$P_B$) = 312.0, $J$(Rh,$P_B$) = 123.8 Hz; *t*Bu$_2$$P_B$ of rotamer R$^1$), 46.6 ppm (d, $J$(Rh,P) = 120.4 Hz; *t*Bu$_2$P of rotamer R$^3$); elemental analysis (%) for $C_{33}H_{54}OP_2ClRh$ (667.1): calcd: C 59.42, H 8.16, Rh 15.42; found: C 59.10, H 7.86, Rh 15.33.

**[RhH$_2$Cl($C_6H_5CH_2CH_2P$*t*Bu$_2$-$\kappa$P)$_2$] (20)**: A suspension of **17** (103 mg, 0.16 mmol) in pentane (7 mL) was stirred under a hydrogen atmosphere (1

bar) for 1 h at room temperature. A light yellow solution was formed which, after the solvent was evaporated in vacuo, gave a light yellow solid; yield 95 mg (93%); m.p. 105 °C (decomp); IR (KBr): $\tilde{\nu}$ = 2138 (br) cm$^{-1}$ (RhH); $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 7.51 (m, 4H; *ortho*-H of $C_6H_5$), 7.20 (m, 4H; *meta*-H of $C_6H_5$), 7.08 (m, 2H; *para*-H of $C_6H_5$), 3.25 (m, 4H; $PCH_2CH_2$), 2.31 (m, 4H; $PCH_2$), 1.28 (virt. t, $N$ = 12.6 Hz, 36H; $PCCH_3$), −22.63 ppm (dt, $J$(Rh,H) = 26.3, $J$(P,H) = 14.7 Hz, 2H; RhH); $^{13}$C NMR (100.6 MHz, $C_6D_6$): $\delta$ = 144.2 (virt. t, $N$ = 13.4 Hz; *ipso*-C of $C_6H_5$), 128.9, 128.8, 126.4 (all s; $C_6H_5$), 35.0 (virt. t, $N$ = 17.2 Hz; $PCCH_3$), 34.4 (s; $PCH_2CH_2$), 30.5 (virt. t, $N$ = 5.7 Hz; $PCCH_3$), 26.2 ppm (virt. t, $N$ = 15.3 Hz; $PCH_2$); $^{31}$P NMR (162.0 MHz, $C_6D_6$): $\delta$ = 65.6 (d, $J$(Rh,P) = 115.3 Hz); elemental analysis (%) for $C_{32}H_{56}P_2ClRh$ (641.1): calcd: C 59.95, H 8.80; found: C 60.40, H 8.66.

**[RhD$_2$Cl(C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-κP)$_2$] ([D$_2$]20)**: A suspension of **17** (84 mg, 0.13 mmol) in pentane (15 mL) was stirred under a $D_2$ atmosphere for 2 h at room temperature. After the solvent was removed in vacuo, the light yellow residue was washed with pentane (2 × 4 mL) and dried; yield 72 mg (85%); m.p. 92 °C (decomp); $^1$H NMR (400 MHz, $C_6D_6$): nearly identical to that of **20** but without the signal at $\delta$ = −22.63 ppm; the $^{13}$C NMR and $^{31}$P NMR spectra are both identical to those of **20**.

**Generation in situ of [RhHCl(C≡CC$_6$H$_5$)(C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-κP)$_2$] (21)**: A solution of **17** (22 mg, 0.03 mmol) in [$D_8$]toluene was treated at −78 °C with phenylacetylene (4 νL, 0.03 mmol) and monitored by NMR spectroscopy. Characteristic data for **21**: $^1$H NMR (200 MHz): $\delta$ = −27.72 ppm (br dt, $J$(Rh,H) = 42.2, $J$(P,H) = 11.6 Hz, 1H; RhH); $^{31}$P NMR (81.0 MHz): $\delta$ = 40.5 ppm (d, $J$(Rh,P) = 119.5 Hz).

***trans*-[RhCl(=C=CHPh)(C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-κP)$_2$] (22)**: Method a: A solution of **17** (146 mg, 0.23 mmol) in toluene (5 mL) was treated at −78 °C with phenylacetylene (25 νL, 0.23 mmol). The solution was slowly warmed to room temperature and stirred for 8 h. A stepwise change of color from yellow to red-brown and then to blue-violet occurred. The solvent was evaporated in vacuo, the residue was dissolved in hexane (1 mL) and the solution was chromatographed on $Al_2O_3$ (neutral, activity grade III). With hexane, an off-white fraction was eluted which was thrown away. With benzene, a blue fraction was eluted which was brought to dryness in vacuo. The oily residue was dissolved in pentane (2 mL) and the solution was stored at −60 °C. A blue-violet solid precipitated, which was filtered, washed with pentane (2 × 1 mL, 0 °C) and dried; yield 133 mg (78%).

Method B: Analogously as described for method A, but using **20** (120 mg, 0.19 mmol) and phenylacetylene (39 νL, 0.38 mmol) as starting materials; time of reaction 12 h; yield 100 mg (72%); m.p. 77 °C (decomp); IR (hexane): $\tilde{\nu}$ = 1646, 1624 und 1598 cm$^{-1}$ (C=C); $^1$H NMR (300 MHz, $C_6D_6$, 313 K): $\delta$ = 7.35 (m, 4H; $C_6H_5$), 7.21–7.05 (m, 10H; $C_6H_5$), 6.86 (m, 1H; *para*-H of =CH$C_6H_5$), 3.23 (m, 4H; $PCH_2CH_2$) 2.53 (m, 4H; $PCH_2$), 1.45 (virt. t, $N$ = 12.5 Hz, 36H; $PCCH_3$), 1.36 ppm (dt, $J$(P,H) = 3.2, $J$(Rh,H) = 1.1 Hz, 1H; Rh=C=CH); $^{13}$C NMR (75.4 MHz, $C_6D_6$, 313 K): $\delta$ = 290.6 (m; Rh=*C*=CH), 143.6 (virt. t, $N$ = 13.4 Hz; *ipso*-C of $CH_2C_6H_5$), 128.7, 128.6, 126.4 (all s; $CH_2C_6H_5$), 127.3, 126.3, 125.3 (all s; =CH$C_6H_5$), 124.8 (t, $J$(P,C) = 2.3 Hz; *ipso*-C of =CH$C_6H_5$), 116.2 (m; Rh=C=*C*H), 35.9 (virt. t, $N$ = 14.3 Hz; P*C*CH$_3$), 33.3 (s, $PCH_2CH_2$), 31.2 (virt. t, $N$ = 4.6 Hz; $PCCH_3$), 23.1 ppm (virt. t, $N$ = 15.3 Hz; $PCH_2$); $^{31}$P NMR (81.0 MHz, $C_6D_6$, 308 K): $\delta$ = 52.5 ppm (d, J(RhP) = 137.3 Hz); $^{31}$P NMR (162.0 MHz, $C_6D_6$, 293 K): $\delta$ = 45.7 ppm (br s); $^{31}$P NMR (162.0 MHz, [$D_8$]toluene, 233 K): $\delta$ = 47.7 ppm (dd, $J$($P_A$,$P_B$) = 345.9, $J$(Rh,$P_A$) = 133.9 Hz; *t*Bu$_2$P$_A$ of rotamer R$^1$), 46.2 (d, $J$(Rh,P) = 135.6 Hz; *t*Bu$_2$P of rotamer R$^2$), 41.8 (d, $J$(Rh,P) = 140.7 Hz; *t*Bu$_2$P of rotamer R$^3$), 41.6 (dd, $J$($P_A$,$P_B$) = 345.9, $J$(Rh,$P_B$) = 137.3 Hz; *t*Bu$_2$P$_B$ of rotamer R$^1$); elemental analysis (%) for $C_{40}H_{60}P_2ClRh$ (741.2): calcd: C 64.82, H 8.16; found: C 64.74, H 8.04.

***trans*-[RhCl(=C=CDPh)(C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-κP)$_2$] ([D$_1$]22)**: A solution of **17** (78 mg, 0.12 mmol) in toluene (3 mL) was treated at −78 °C with a solution of DC≡CPh (13 mg, 0.12 mmol) in hexane (2 mL). The solution was slowly warmed to room temperature and then stirred for 8 h. The solvent was evaporated in vacuo and the residue investigated by NMR spectrocopy. The $^1$H NMR spectrum is nearly identical to that of **22** but without the signal at $\delta$ = 1.36 ppm; the $^{13}$C NMR and $^{31}$P NMR are both identical to those of **22**. $^2$H NMR (61.42 MHz, $C_6H_6$): $\delta$ = 1.40 ppm (s; Rh=C=CD).

***trans*-[RhCl(=C=CH*t*Bu)(C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-κP)$_2$] (23)**: Analogously as described for **22**, with **17** (135 mg, 0.21 mmol) and 3,3-dimethylbutyne (39 μL, 0.32 mmol) as starting materials; time of reaction four days. A blue solid was isolated; yield 125 mg (82%); m.p. 91 °C (decomp); IR (KBr): $\tilde{\nu}$ = 1668, 1641, 1602 cm$^{-1}$ (C=C); $^1$H NMR (200 MHz, $C_6D_6$, 293 K): $\delta$ = 7.45–7.03 (m, 10H; $C_6H_5$), 3.20 (m, 4H; $PCH_2CH_2$) 2.54 (m, 4H; $PCH_2$), 1.50 (virt. t, $N$ = 12.1 Hz, 36H; $PCCH_3$), 0.90 (s, 9H; =CHC(C$H_3$)$_3$), −0.30 ppm (dt, $J$(P,H) = 3.3, $J$(Rh,H) = 1.5 Hz, 1H; Rh=C=CH); $^{13}$C NMR (75.4 MHz, $C_6D_6$, 323 K): $\delta$ = 286.2 (m; Rh=*C*=CH), 143.6 (virt. t, $N$ = 13.2 Hz; *ipso*-C of $C_6H_5$), 128.7, 128.5, 126.3 (all s; $C_6H_5$), 120.4 (m; Rh=C=*C*H), 36.3 (d virt. t, $N$ = 13.6, $J$(Rh,C) = 0.8 Hz; P*C*CH$_3$), 33.0 (s; $PCH_2CH_2$), 32.5 (t, $J$(P,C) = 1.1 Hz; =CHC(CH$_3$)$_3$), 31.5 (virt. t, $N$ = 5.1 Hz; P*C*CH$_3$), 25.3 (t, $J$(P,C) = 1.5 Hz; =CH*C*(CH$_3$)$_3$), 22.4 ppm (m; $PCH_2$); $^{31}$P NMR (81.0 MHz, $C_6D_6$, 313 K): $\delta$ = 45.8 (d, $J$(Rh,P) = 142.4 Hz); $^{31}$P NMR (81.0 MHz, $C_6D_6$, 293 K): $\delta$ = 44.7 ppm (br d).; elemental analysis (%) for $C_{38}H_{64}P_2ClRh$ (721.2): calcd: C 63.28, H 8.94; found: C 63.14, H 8.99.

**[RhHCl$_2$(C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-κP)$_2$] (24)**: A slow stream of gaseous HCl was passed through a suspension of **17** (124 mg, 0.19 mmol) in pentane (6 mL) for 10 s at room temperature. An orange oil precipitated. The solvent was evaporated in vacuo and the oily residue was extracted with diethyl ether (2 × 7 mL each). The combined extracts were concentrated in vacuo as long as an orange precipitate was formed. This was filtered, washed with pentane (2 × 6 mL) and dried; yield 116 mg (90%); m.p. 134 °C (decomp); IR (Nujol): $\tilde{\nu}$ = 2361, 2341 cm$^{-1}$ (RhH); $^1$H NMR (400 MHz, $C_6D_6$, 293 K): $\delta$ = 7.53 (m, 4H; *ortho*-H of $C_6H_5$), 7.20 (m, 4H; *meta*-H of $C_6H_5$), 7.09 (m, 2H; *para*-H of $C_6H_5$), 3.10 (br s, 8H; P$CH_2CH_2$), 1.43 (br s, 36H; $PCCH_3$), −30.84 ppm (dt, $J$(Rh,H) = 32.1, $J$(P,H) = 12.9 Hz, 1H; RhH); $^1$H NMR (300 MHz, $C_6D_6$, 333 K): $\delta$ = 7.49 (m, 4H; *ortho*-H of $C_6H_5$), 7.20 (m, 4H; *meta*-H of $C_6H_5$), 7.08 (m, 2H; *para*-H of $C_6H_5$), 3.13 (m, 4H; $PCH_2CH_2$) 2.47 (m, 4H; $PCH_2$), 1.46 (virt. t, $N$ = 12.8 Hz, 36H; $PCCH_3$), −30.77 ppm (dt, $J$(Rh,H) = 32.5, $J$(P,H) = 12.4 Hz, 1H; RhH); $^{13}$C NMR (100.6 MHz, $C_6D_6$, 293 K): $\delta$ = 143.9 (virt. t, $N$ = 14.2 Hz; *ipso*-C of $C_6H_5$), 128.9, 128.8, 126.5 (all s; $C_6H_5$), 36.2 (m; P*C*CH$_3$), 33.5 (s; $PCH_2CH_2$), 31.4 (br s; $PCCH_3$), 22.6 ppm (m; $PCH_2$); $^{13}$C NMR (75.4 MHz, $C_6D_6$, 333 K): $\delta$ = 143.9 (virt. t, $N$ = 13.5 Hz; *ipso*-C of $C_6H_5$), 128.9, 128.8, 126.4 (all s; $C_6H_5$), 36.3 (virt. t, $N$ = 15.6 Hz; P*C*CH$_3$), 33.5 (s; $PCH_2CH_2$), 31.5 (virt. t, $N$ = 4.4 Hz; $PCCH_3$), 22.6 ppm (virt. t, $N$ = 17.8 Hz; $PCH_2$); $^{31}$P NMR (162.0 MHz, $C_6D_6$, 293 K): $\delta$ = 47.9 ppm (d, $J$(Rh,P) = 96.6 Hz); $^{31}$P NMR (162.0 MHz, [$D_8$]toluene, 243 K): $\delta$ = 47.3 (d, $J$(Rh,P) = 96.6 Hz; *t*Bu$_2$P of rotamer R$^1$), 46.6 ppm (d, $J$(Rh,P) = 96.6 Hz; *t*Bu$_2$P of rotamer R$^2$); elemental analysis (%) for $C_{32}H_{55}P_2Cl_2Rh$ (675.6): calcd: C 56.89, H 8.21, Rh 15.23; found: C 56.72, H 7.97, Rh 15.02.

**[RhDCl$_2$(C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-κP)$_2$] ([D$_1$]24)**: A slow stream of DCl was passed for 30 s through a suspension of **17** (86 mg, 0.13 mmol) in pentane (6 mL) at room temperature. The solvent was evaporated in vacuo, the remaining orange solid was washed with pentane (2 × 5 mL) and dried; yield 72 mg (85%); m.p. 101 °C (decomp); $^1$H NMR (400 MHz, $C_6D_6$): nearly identical to that of **24**, but without the signal at $\delta$ = −30.77 ppm; the $^{13}$C NMR and $^{31}$P NMR are both identical to those of **24**.

**Reaction of compound 32 with NEt$_3$**: A solution of **24** (34 mg, 0.05 mmol) in $C_6D_6$ (0.5 mL) was treated with $NEt_3$ (140 μL, 1.00 mmol) and stirred for 5 min at room temperature. The $^{31}$P NMR spectrum of the solution revealed that the starting materials reacted exclusively to give **17**.

**[(η$^6$-C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-κP)Rh(C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-κP)]PF$_6$ (25a)**: A solution of **17** (136 mg, 0.21 mmol) in toluene (6 mL) was treated at −60 °C with a solution of $AgPF_6$ (54 mg, 0.21 mmol) in diethyl ether (2 mL). While the solution was warmed to room temperature, an off-white solid precipitated and a change of color from yellow to brown occurred. The solution was filtered, and the filtrate was brought to dryness in vacuo. The residue was extracted with $CH_2Cl_2$ (2 × 4 mL) and the solvent was evaporated from the combined extracts. The residue was dissolved in acetone (1 mL) and the solution was layered with diethyl ether (6 mL). A pale brown solid precipitated which was separated from the mother liquor, washed with diethyl ether (2 × 5 mL each) and dried; yield 138 mg (88%); m.p. 107 °C (decomp); $\Lambda_M$ = 64 cm$^2\Omega^{-1}$mol$^{-1}$; $^1$H NMR (200 MHz, [$D_6$]acetone): $\delta$ = 7.37–7.05 (m, 9H; $C_6H_5$), 6.12 (m, 1H; *para*-H of η$^6$-$C_6H_5$), 3.20 (m, 2H; $PCH_2CH_2$), 2.71 (m, 2H; $PCH_2$), 2.53 (m, 2H; $PCH_2CH_2$), 2.33 (m, 2H; $PCH_2$), 1.51 (d, $J$(P,H) = 12.8 Hz, 18H; $PCCH_3$), 1.21 ppm (d, $J$(P,H) = 13.5 Hz, 18H; $PCCH_3$); $^{13}$C NMR (50.3 MHz, [$D_6$]acetone): $\delta$ = 142.5 (d, $J$($P_B$,C) = 9.3 Hz; *ipso*-C of $C_6H_5$), 129.4, 129.1, 127.2 (all s; $C_6H_5$), 111.5 (ddd, $J$($P_A$,C) = 4.7, $J$($P_B$,C) = 9.2, $J$(Rh,C) = 3.7 Hz; *ipso*-C of η$^6$-$C_6H_5$), 105.7 (br s, η$^6$-$C_6H_5$), 88.7 (d, $J$($P_A$,C) = 10.2 Hz; *para*-C of η$^6$-$C_6H_5$), 40.8 (dd, $J$($P_A$,C) = 25.0, $J$($P_B$,C) = 2.0 Hz; η$^6$-$C_6H_5CH_2CH_2$), 39.8 (m;

$C_6H_5CH_2CH_2$), 38.9 (d, $J(P_B,C) = 15.7$ Hz; $P_BCCH_3$), 36.4 (dd, $J(P_A,C) = 10.2$, $J(Rh,C) = 2.8$ Hz; $P_ACCH_3$), 34.7 (m; $C_6H_5CH_2CH_2$), 31.7 (d, $J(P,C) = 4.6$ Hz; $PCCH_3$), 31.4 (d, $J(P,C) = 4.6$ Hz; $PCCH_3$), 30.6 ppm (s; $C_6H_5CH_2$); $^{31}$P NMR (81.0 MHz, [D$_6$]acetone): $\delta = 81.5$ (dd, $J(Rh,P_A) = 211.1$, $J(P_A,P_B) = 15.3$ Hz; $tBu_2P_A$), 68.6 (dd, $J(Rh,P_B) = 203.4$, $J(P_A,P_B) = 15.3$ Hz; $tBu_2P_B$), −142.7 ppm (sept, $J(F,P) = 707.0$ Hz; $PF_6$); $P_A$ corresponds to the phosphorus atom of the chelating ligand and $P_B$ to the phosphorus atom of the monodentate ligand; elemental analysis (%) for $C_{32}H_{54}F_6P_3Rh$ (748.6): calcd: C 51.34, H 7.27; found: C 51.37, H 7.34.

**[(η$^6$-$C_6H_5CH_2CH_2P$*t*$Bu_2$-κP)Rh($C_6H_5CH_2CH_2P$*t*$Bu_2$-κP)]$BF_4$ (25b)**: A solution of **17** (262 mg, 0.41 mmol) in toluene (5 mL) was treated at −60 °Cwith a 54 % solution von $HBF_4$ in diethyl ether (29 μL, 0.21 mmol). While the reaction mixture was warmed to room temperature, a change of color from yellow to orange-red occurred. The solvent was evaporated in vacuo and the oily residue was extracted with diethyl ether (3 × 7 mL). The combined extracts were brought to dryness in vacuo to give an orange solid which was washed with pentane (2 × 6 mL) and dried. The solid was characterized as **24** by spectroscopic techniques; yield 126 mg (46 %). The residue which was left behind after the extraction with ether was dissolved in acetone (2 mL) and under continuous stirring diethyl ether (7 mL) was added. A brownish solid of composition **25b** precipitated which was separated from the mother liquor, washed with diethyl ether (2 × 5 mL) and dried; yield 122 mg (43 %); m.p. 105 °C (decomp); $\Lambda_M = 65$ cm$^2\,\Omega^{-1}$mol$^{-1}$; $^1$H NMR (400 MHz, [D$_6$]acetone): $\delta = 7.29-7.12$ (m, 9H; $C_6H_5$), 6.14 (m, 1H; *para*-H of η$^6$-$C_6H_5$), 3.21, 2.54 (both m, 2H each; $PCH_2CH_2$), 2.73, 2.34 (both m, 2H each; $PCH_2$), 1.52, 1.22 ppm (both d, $J(P,H) = 13.2$ Hz, 18H each; $PCCH_3$); $^{13}$C NMR (100.6 MHz, [D$_6$]acetone): $\delta = 142.5$ (d, $J(P_B,C) = 8.6$ Hz, *ipso*-C of $C_6H_5$), 129.4, 129.0, 127.3 (all s; $C_6H_5$), 111.5 (ddd, $J(P_A,C) = 4.8$, $J(P_B,C) = 8.6$, $J(Rh,C) = 3.8$ Hz; in $^{13}$C{$^{31}$P} d, $J(Rh,C) = 3.8$ Hz; in $^{13}$C{$^{31}P_A$} dd, $J(P_B,C) = 8.6$, $J(Rh,C) = 3.8$ Hz, *ipso*-C of η$^6$-$C_6H_5$), 105.8, 105.6 (both br s; η$^6$-$C_6H_5$), 88.8 (d, $J(P_A,C) = 9.5$ Hz, *para*-C of η$^6$-$C_6H_5$), 40.9 (dd, $J(P_A,C) = 24.8$, $J(P_B,C) = 1.9$ Hz; η$^6$-$C_6H_5CH_2CH_2$), 39.8, 34.7 (both m; $C_6H_5CH_2CH_2$), 38.9 (d, $J(P_B,C) = 15.3$ Hz; $P_BCCH_3$), 36.4 (dd, $J(P_A,C) = 10.5$, $J(Rh,C) = 2.9$ Hz; $P_ACCH_3$), 31.7 (d, $J(P,C) = 4.8$ Hz; $PCCH_3$), 31.4 (d, $J(P,C) = 3.8$ Hz; $PCCH_3$), 30.6 ppm (s; η$^6$-$C_6H_5CH_2$); $^{31}$P NMR (162.0 MHz, [D$_6$]acetone): $\delta = 80.1$ (dd, $J(Rh,P_A) = 211.9$, $J(P_A,P_B) = 15.3$ Hz; $tBu_2P_A$), 67.2 ppm (dd, $J(Rh,P_B) = 205.1$, $J(P_A,P_B) = 15.3$ Hz; $tBu_2P_B$); $P_A$ corresponds to the phosphorus atom of the chelating ligand and $P_B$ to the phosphorus atom of the monodentate ligand; elemental analysis (%) for $C_{32}H_{54}BF_4P_2Rh$ (690.4): calcd: C 55.67, H 7.88; found: C 55.91, H 7.61.

**[(η$^6$-$C_6H_5CH_2CH_2P$*t*$Bu_2$-κP)Rh($C_2H_4$)]$PF_6$ (27)**: A solution of **26** (245 mg, 0.40 mmol) in $CH_2Cl_2$ (2 mL) was heated under an ethene atmosphere for 1 h at 75 °C. After the solution was cooled to room temperature, diethyl ether (8 mL) was added, which led to the precipitation of an orange solid. The mother liquor was decanted, and the solid was washed with diethyl ether (5 mL). This procedure was repeated twice. The combined orange solids were finally washed with diethyl ether (2 × 5 mL) and dried; yield 181 mg (86 %); m.p. 178 °C (decomp); $\Lambda_M = 119$ cm$^2\,\Omega^{-1}$mol$^{-1}$; $^1$H NMR (200 MHz, [D$_6$]acetone): $\delta = 7.47-7.30$ (m, 4H; $C_6H_5$), 5.52 (m, 1H; $C_6H_5$), 3.22 (br s, 4H; $C_2H_4$), 2.99–2.63 (m, 4H; $PCH_2CH_2$), 1.31 ppm (d, $J(P,H) = 13.9$ Hz, 18H; $PCCH_3$); $^{13}$C NMR (50.3 MHz, [D$_6$]acetone): $\delta = 123.1$ (dd, $J(P,C) = J(Rh,C) = 4.6$ Hz; *ipso*-C of $C_6H_5$), 109.5 (s; $C_6H_5$), 105.2 (d, $J(P,C) = 2.8$ Hz, $C_6H_5$), 93.5 (dd, $J(P,C) = 11.1$, $J(Rh,C) = 2.8$ Hz; *para*-C of $C_6H_5$), 42.2 (d, $J(Rh,C) = 13.9$ Hz; $C_2H_4$), 41.0 (d, $J(P,C) = 25.0$ Hz; $PCH_2$), 37.1 (dd, $J(P,C) = 16.7$, $J(Rh,C) = 1.9$ Hz; $PCCH_3$), 31.8 (s; $PCH_2CH_2$), 30.1 ppm (s; $PCCH_3$); $^{31}$P NMR (81.0 MHz, [D$_6$]acetone): $\delta = 98.7$ (d, $J(Rh,P) = 183.1$ Hz; $tBu_2P$), −144.3 ppm (sept, $J(F,P) = 707.0$ Hz; $PF_6$); elemental analysis (%) for $C_{18}H_{31}F_6P_2Rh$ (526.3): calcd: C 41.08, H 5.94, Rh 19.55; found: C 40.99, H 5.92, Rh 19.29.

**[(η$^6$-$C_6H_5CH_2CH_2P$*t*$Bu_2$-κP)Rh(SbiPr$_3$)]$PF_6$ (28)**: A solution of **26** (103 mg, 0.17 mmol) in $CH_2Cl_2$ (3 mL) was treated with $SbiPr_3$ (282 νL, 1.36 mmol) and stirred for 8 h at room temperature. A change of color from yellow to red-brown occurred. After the solvent was evaporated in vacuo, the oily residue was washed with pentane (2 × 5 mL) and then dissolved in acetone (3 mL). Addition of diethyl ether (10 mL) to the solution led to the precipitation of a pale brown solid, which was filtered, washed with diethyl ether (2 × 5 mL) and acetone (2 × 5 mL) and dried; yield 107 mg (84 %); m.p. 123 °C (decomp); $\Lambda_M = 69$ cm$^2\,\Omega^{-1}$mol$^{-1}$; $^1$H NMR (200 MHz, $CD_2Cl_2$): $\delta = 6.91-6.78$ (m, 4H; $C_6H_5$), 5.58 (m, 1H; $C_6H_5$), 2.64 (m, 2H; $PCH_2$), 2.42 (m, 2H; $PCH_2CH_2$), 2.21 (sept, $J(H,H) = 7.3$ Hz, 3H; $SbCHCH_3$), 1.34 (d, $J(H,H) = 7.3$ Hz, 18H; $SbCHCH_3$), 1.25 ppm (d, $J(P,H) = 14.3$ Hz, 18H; $PCCH_3$); $^{13}$C NMR (50.3 MHz, $CD_2Cl_2$): $\delta = 109.2$ (dd, $J(P,C) = 5.2$, $J(Rh,C) = 4.5$ Hz; *ipso*-C of $C_6H_5$), 101.6 (br s, $C_6H_5$), 101.4 (d, $J(Rh,C) = 3.2$ Hz; $C_6H_5$), 86.4 (dd, $J(P,C) = 9.7$, $J(Rh,C) = 2.0$ Hz; *para*-C of $C_6H_5$), 40.1 (d, $J(P,C) = 24.7$ Hz; $PCH_2$), 34.7 (dd, $J(P,C) = 17.5$, $J(Rh,C) = 2.0$ Hz; $PCCH_3$), 31.5 (s; $PCH_2CH_2$), 29.9 (d, $J(P,C) = 4.6$ Hz; $PCCH_3$), 22.3 (d, $J(Rh,C) = 3.2$ Hz; $SbCHCH_3$), 21.6 ppm (s; $SbCHCH_3$); $^{31}$P NMR (81.0 MHz, $CD_2Cl_2$): $\delta = 116.9$ (d, $J(Rh,P) = 188.2$ Hz; $tBu_2P$), −144.0 ppm (sept, $J(F,P) = 711.3$ Hz; $PF_6$); elemental analysis (%) for $C_{25}H_{48}F_6P_2RhSb$ (749.3): calcd: C 40.08, H 6.46, Rh 13.74; found: C 39.67, H 6.19, Rh 13.91.

**Generation of [$RhH_2$(O=$CMe_2$)$_3$($C_6H_5CH_2CH_2P$*i*$Pr_2$-κP)]$PF_6$ (30) and [$RhH_2${O=$C(CD_3)_2$}$_3$($C_6H_5CH_2CH_2P$*i*$Pr_2$-κP)]$PF_6$ ([$D_{18}$]30)**: A solution of **29** (102 mg, 0.20 mmol) in acetone (5 mL) was stirred under a hydrogen atmosphere (1 bar) for 12 h at room temperature. A smooth change of color from yellow to pale brown occurred. The $^{31}$P NMR spectrum of the solution displays a single resonance at $\delta = 80.8$ ppm (d, J(Rh,P) = 162.8 Hz) which indicates that compound **30** is exclusively formed. Attempts to isolate **30** by addition of pentane or ether to the solution in acetone failed. If the reaction was carried out in [D$_6$]acetone (0.5 mL) with **29** (45 mg, 0.09 mmol) as starting material, the deuterated compound **[$D_{18}$]30** was obtained. Spectroscopic data of **[$D_{18}$]30**: $^1$H NMR (200 MHz, [D$_6$]acetone): $\delta = 7.34-7.11$ (m, 5H; $C_6H_5$), 2.90 (m, 2H; $PCH_2CH_2$), 2.28–1.97 (m, 4H; $PCHCH_3$ and $PCH_2$), 1.18 (dd, $J(P,H) = 15.8$, $J(H,H) = 6.9$ Hz, 6H; $PCHCH_3$), 1.16 (dd, $J(P,H) = 14.8$, $J(H,H) = 6.9$ Hz, 6H; $PCHCH_3$), −23.0 ppm (dd, $J(Rh,H) = J(P,H) = 28.6$ Hz, 2H; RhH); $^{13}$C NMR (50.3 MHz, [D$_6$]acetone): $\delta = 210.4$ (br; C=O), 143.1 (d, $J(P,C) = 13.0$ Hz; *ipso*-C of $C_6H_5$), 129.3, 128.7, 126.9 (all s; $C_6H_5$), 31.7 (s; $PCH_2CH_2$), 26.7 (d, $J(P,C) = 25.9$ Hz; $PCH_2$), 25.8 (dd, $J(P,C) = 33.3$, $J(Rh,C) = 1.9$ Hz; $PCHCH_3$), 18.9, 18.7 ppm (both s; $PCHCH_3$); signal for $CD_3$ carbon atom not exactly located; $^{31}$P NMR (81.0 MHz, [D$_6$]acetone): $\delta = 80.8$ (d, $J(Rh,P) = 162.8$ Hz; *i*$Pr_2P$), −142.7 ppm (sept, $J(F,P) = 707.0$ Hz; $PF_6$).

**Generation of [$RhH_2${O=$C(CD_3)_2$}$_3$($C_6H_5CH_2CH_2P$*t*$Bu_2$-κP)]$PF_6$ ([$D_{18}$]31)**: A solution of **27** (39 mg, 0.07 mmol) in [D$_6$]acetone (0.5 mL) was stirred under a hydrogen atmosphere (1 bar) for 12 h at room temperature. The generated product was characterized spectroscopically; IR ([D$_6$]acetone): $\tilde{\nu} = 2143$ (br) cm$^{-1}$ (RhH); $^1$H NMR (200 MHz, [D$_6$]acetone, 293 K): $\delta = 7.40-6.95$ (m, 5H; $C_6H_5$), 3.07 (m, 2H; $PCH_2CH_2$), 2.51 (br s, 2H; $PCH_2$), 1.32 (d, $J(P,H) = 13.8$ Hz, 18H; $PCCH_3$), −23.24 ppm (br s, 2H; RhH); $^1$H NMR (400 MHz, [D$_6$]acetone, 263 K): $\delta = 7.32-7.16$ (m, 5H; $C_6H_5$), 3.05 (m, 2H; $PCH_2CH_2$), 2.19 (m, 2H; $PCH_2$), 1.29 (d, $J(P,H) = 13.7$ Hz, 18H; $PCCH_3$), −23.25 ppm (dd, $J(Rh,H) = J(P,H) = 27.9$ Hz, 2H; RhH); $^{13}$C NMR (100.6 MHz, [D$_6$]acetone, 263 K): $\delta = 210.2$ (s; C=O), 143.5 (d, $J(P,C) = 14.3$ Hz, *ipso*-C of $C_6H_5$), 129.2, 128.7, 126.8 (all s; $C_6H_5$), 35.8 (d, $J(P,C) = 26.7$ Hz; $PCCH_3$), 32.9 (s; $PCH_2$), 29.7 (s; $PCCH_3$), 26.0 ppm (d, $J(P,C) = 21.9$ Hz, $PCH_2$), signal for $CD_3$ carbon atom not exactly located; $^{31}$P NMR (81.0 MHz, [D$_6$]acetone, 263 K): $\delta = 94.4$ (br d, $J(Rh,P) = 165.7$ Hz; $tBu_2P$), −144.2 ppm (sept, $J(F,P) = 708.4$ Hz; $PF_6$).

**[(η$^6$-$C_6H_5CH_2CH_2P$*t*$Bu_2$-κP)$RhH_2$]$PF_6$ (32)**: A solution of **27** (125 mg, 0.24 mmol) in acetone (6 mL) was stirred under a hydrogen atmosphere (1 bar) for 12 h at room temperature. A smooth change of color from orange-red to brown-yellow occurred. The solution was concentrated in vacuo to about 2 mL and layered with diethyl ether (12 mL). After it was stored for 3 h, a brown solid precipitated, which was filtered, washed with diethyl ether (2 × 5 mL) and with pentane (2 × 5 mL) and dried; yield 100 mg (83 %); m.p. 55 °C (decomp); $\Lambda_M = 88$ cm$^2\,\omega^{-1}$mol$^{-1}$; IR (KBr): $\tilde{\nu} = 2111$, 2073 cm$^{-1}$ (RhH); $^1$H NMR (200 MHz, $CD_2Cl_2$): $\delta = 7.15$ (m, 2H; *meta*-H of $C_6H_5$), 6.87 (m, 2H; *ortho*-H of $C_6H_5$), 6.42 (m, 1H; *para*-H of $C_6H_5$), 3.16–2.81 (m, 4H; $PCH_2CH_2$), 1.26 (d, $J(P,H) = 14.8$ Hz, 18H; $PCCH_3$), −12.15 ppm (dd, $J(Rh,H) = 26.6$, $J(P,H) = 19.7$ Hz, 2H; RhH); $^{13}$C NMR (50.3 MHz, $CD_2Cl_2$): $\delta = 136.2$ (dd, $J(P,C) = 6.5$, $J(Rh,C) = 2.0$ Hz; *ipso*-C of $C_6H_5$), 110.7, 105.8 (both s; $C_6H_5$), 96.9 (d, $J(P,C) = 7.8$ Hz; *para*-C of $C_6H_5$), 41.8 (d, $J(P,C) = 22.7$ Hz; $PCH_2$), 36.5 (dd, $J(P,C) = 23.4$, $J(Rh,C) = 2.0$ Hz; $PCCH_3$), 32.5 (s; $PCH_2CH_2$), 29.1 ppm (d, $J(P,C) = 3.3$ Hz; $PCCH_3$); $^{31}$P NMR (81.0 MHz, $CD_2Cl_2$): $\delta = 133.1$ (d, $J(Rh,P) = 155.1$ Hz; $tBu_2P$), −143.9 ppm (sept, $J(F,P) = 712.1$ Hz; $PF_6$); elemental analysis (%) for $C_{16}H_{29}F_6P_2Rh$ (500.3): calcd: C 38.42, H 5.84; found: C 37.99, H 5.47.

**[$RhH_2$(O=$CMe_2$)$_3$(*Pi*$Pr_3$)]$PF_6$ (34)**: A solution of **33** (120 mg, 0.23 mmol) in acetone (5 mL) was stirred under a hydrogen atmosphere for 5 min at

room temperature. A gradual change of color from yellow to light yellow occurred. The solution was concentrated to about 1 mL in vacuo and diethyl ether (10 mL) was added. A brownish solid precipitated, which was filtered, washed with diethyl ether (2 × 5 mL) and pentane (2 × 5 mL) and dried; yield 117 mg (87%); m.p. 22 °C (decomp); $\Lambda_M = 94\ cm^2\,\Omega^{-1}mol^{-1}$; IR ($CH_2Cl_2$): $\tilde{\nu} = 2134$ (br, RhH), 1712, 1673 $cm^{-1}$ (C=O); $^1H$ NMR (200 MHz, $CD_2Cl_2$, 293 K): $\delta = 2.31$ (s, 18H; O=C($CH_3$)$_2$), 2.13 (m, 3H; PC*H*$CH_3$), 1.18 (dd, $J$(P,H) = 15.3, $J$(H,H) = 6.6 Hz, 18H; PCHC*H*$_3$), −23.30 ppm (dd, $J$(Rh,H) = 31.2, $J$(P,H) = 25.5 Hz, 2H; RhH); $^{13}C$ NMR (100.6 MHz, $CD_2Cl_2$, 253 K): $\delta = 215.6$ (br s; C=O), 31.7 (s; O=C(*C*$H_3$)$_2$), 24.8 (d, $J$(P,C) = 29.6 Hz; P*C*HCH$_3$), 19.1 (s; PCH*C*H$_3$); $^{31}P$ NMR (81.0 MHz, $CD_2Cl_2$, 293 K): $\delta = 87.0$ (d, $J$(Rh,P) = 157.7 Hz; P*i*Pr$_3$), −144.0 ppm (sept, $J$(F,P) = 712.1 Hz; $PF_6$); elemental analysis (%) for $C_{18}H_{41}F_6O_3P_2Rh$ (584.4): calcd: C 37.00, H 7.07; found: C 34.94, H 6.53.

**[(η⁶-$C_6H_6$)$RhH_2$(P*i*Pr$_3$)]$PF_6$ (35)**: A solution of **34** (103 mg, 0.18 mmol) in $CH_2Cl_2$ (3 mL) was treated with excess benzene (5 mL) and stirred for 5 min at room temperature. After the solution was concentrated to about 2 mL in vacuo, ether (12 mL) was added. A pale brown solid precipitated, which was filtered, washed with diethyl ether (5 mL) and pentane (5 mL) and dried; yield 68 mg (79%); m.p. 71 °C (decomp); $\Lambda_M = 78\ cm^2\,\Omega^{-1}mol^{-1}$; IR (KBr): $\tilde{\nu} = 2103\ cm^{-1}$ (RhH); $^1H$ NMR (200 MHz, $CD_2Cl_2$): $\delta = 6.99$ (s, 6H; $C_6H_6$), 2.09 (m, 3H; PC*H*$CH_3$), 1.14 (dd, $J$(P,H) = 15.8, $J$(H,H) = 6.9 Hz, 18 Hz; PCHC*H*$_3$), −14.54 ppm (dd, $J$(Rh,H) = 28.1, $J$(P,H) = 24.1 Hz, 2H; RhH); $^{13}C$ NMR (50.3 MHz, $CD_2Cl_2$): $\delta = 107.7$ (s; $C_6H_6$), 28.2 (dd, $J$(P,C) = 29.9, $J$(Rh,C) = 1.3 Hz; P*C*HCH$_3$), 20.0 ppm (s; PCHC$H_3$); $^{31}P$ NMR (81.0 MHz, $CD_2Cl_2$): $\delta = 96.5$ (d, $J$(Rh,P) = 142.4 Hz; P*i*Pr$_3$), −143.9 ppm (sept, $J$(F,P) = 712.1 Hz; $PF_6$); elemental analysis (%) for $C_{15}H_{29}F_6P_2Rh$ (488.2): calcd: C 36.90, H 5.99; found: C 36.29, H 5.60.

**[Rh($C_8H_{12}$)(O=C$Me_2$)($C_6H_5CH_2CH_2PiPr_2$-κ-P)]$BF_4$ (37)**: A suspension of **36** (103 mg, 0.21 mmol) in acetone (6 mL) was treated with a solution of [$HL^1$]$BF_4$ (132 mg, 0.43 mmol) in acetone (2 mL) and stirred for 5 min at room temperature. The solvent was evaporated in vacuo and the orange oily residue layered with diethyl ether (5 mL). After storing for 3 h, an orange solid was formed which was washed with diethyl ether (6 × 20 mL each, 0 °C) and dried; yield 174 mg (71%); m.p. 107 °C (decomp); $\Lambda_M = 103\ cm^2\,\Omega^{-1}mol^{-1}$; IR ($CH_2Cl_2$): $\tilde{\nu} = 1653\ cm^{-1}$ (C=O); $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta = 7.32-7.17$ (m, 5H; $C_6H_5$), 5.05, 3.97 (both m, 2H each; =CH of $C_8H_{12}$), 2.92 (m, 2H; PC$H_2$C*H*$_2$), 2.58–2.37 (m, 4H; $CH_2$ of $C_8H_{12}$), 2.24 (m, 2H; PC*H*$CH_3$), 2.05 (m, 4H; $CH_2$ of $C_8H_{12}$), 1.88 (m, 2H; $PCH_2$), 1.41 (dd, $J$(P,H) = 15.7, $J$(H,H) = 7.2 Hz, 6H; PCHC*H*$_3$), 1.39 ppm (dd, $J$(P,H) = 13.7, $J$(H,H) = 6.9 Hz, 6H; PCHC*H*$_3$); $^{13}C$ NMR (100.6 MHz, $CD_2Cl_2$): $\delta = 210.2$ (s; C=O), 142.8 (d, $J$(P,C) = 10.5 Hz; *ipso*-C of $C_6H_5$), 129.4, 128.7, 127.1 (all s; $C_6H_5$), 105.0 (dd, $J$(P,C) = 8.6, $J$(Rh,C) = 7.6 Hz; =CH of $C_8H_{12}$), 70.2 (d, $J$(Rh,C) = 14.3 Hz; =CH of $C_8H_{12}$), 33.7 (d, $J$(P,C) = 2.9 Hz; $CH_2$ of $C_8H_{12}$), 31.3 (d, $J$(P,C) = 2.8 Hz; P$CH_2$*C*$H_2$), 28.3 (s; $CH_2$ of $C_8H_{12}$), 23.9 (d, $J$(P,C) = 21.0 Hz; P*C*HCH$_3$), 20.0 (d, $J$(P,C) = 17.2 Hz; $PCH_2$), 19.7 ppm (d, $J$(P,C) = 2.9 Hz; PCH*C*H$_3$), 19.2 (s; PCH*C*H$_3$); signal for the $CH_3$ carbon atoms of acetone not exactly located; $^{31}P$ NMR (81.0 MHz, $CD_2Cl_2$): $\delta = 30.4$ (d, $J$(Rh,P) = 144.1 Hz); elemental analysis (%) for $C_{22}H_{41}BF_4OPRh$ (578.3): calcd: C 51.93, H 7.15; found: C 51.75, H 7.37.

**[Rh($C_8H_{12}$)($C_6H_5OCH_2CH_2PtBu_2$-κ²*O*,*P*)]$BF_4$ (39)**: A suspension of **36** (134 mg, 0.28 mmol) in acetone (6 mL) was treated with a solution of **38** (196 mg, 0.55 mmol) in acetone (4 mL) and stirred for 5 min at room temperature. A clear yellow solution resulted which was concentrated to about 2 mL in vacuo. Addition of diethyl ether (10 mL) led to the precipitation of a yellow solid, which was filtered, washed with diethyl ether (2 × 5 mL) and with pentane (2 × 5 mL) and dried; yield 243 mg (78%); m.p. 176 °C (decomp); $\Lambda_M = 132\ cm^2\,\Omega^{-1}mol^{-1}$; $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta = 7.45$ (m, 2H; *meta*-H of $C_6H_5$), 7.31 (m, 1H; *para*-H of $C_6H_5$), 7.22 (m, 2H; *ortho*-H of $C_6H_5$), 4.48 (m, 4H; =CH of $C_8H_{12}$), 4.45 (dt, $J$(P,H) = 15.6, $J$(H,H) = 6.7 Hz, 2H; P$CH_2$C*H*$_2$), 2.47, 2.30 (both m, 2 H each; $CH_2$ of $C_8H_{12}$), 2.14 (dt, $J$(P,H) = 8.5, $J$(H,H) = 6.7 Hz, 2H; $PCH_2$), 2.02, 1.83 (both m, 2 H each; $CH_2$ of $C_8H_{12}$), 1.47 ppm (d, $J$(P,H) = 13.5 Hz, 18H; PC$CH_3$); $^{13}C$ NMR (100.6 MHz, $CD_2Cl_2$): $\delta = 157.8$ (s; *ipso*-C of $C_6H_5$), 130.7, 127.7, 120.9 (all s; $C_6H_5$), 104.9 (dd, $J$(P,C) = 9.5, $J$(Rh,C) = 7.6 Hz; =CH of $C_8H_{12}$), 82.8 (s; P$CH_2$C$H_2$), 68.0 (d, $J$(Rh,C) = 15.3 Hz; =CH of $C_8H_{12}$), 36.6 (dd, $J$(P,C) = 13.4, $J$(Rh,C) = 1.9 Hz; P*C*CH$_3$), 33.1 (d, $J$(P,C) = 1.9 Hz; $CH_2$ of $C_8H_{12}$), 29.9 (d, $J$(P,C) = 3.8 Hz; PC*C*H$_3$), 27.2 (s; $CH_2$ of $C_8H_{12}$), 21.3 ppm (d, $J$(P,C) = 16.2 Hz; $PCH_2$); $^{31}P$ NMR (162.0 MHz, $CD_2Cl_2$): $\delta = 64.2$ ppm (d, $J$(Rh,P) = 141.7 Hz); elemental analysis (%) for $C_{24}H_{39}BF_4OPRh$ (564.3): calcd: C 51.09, H 6.97; found: C 51.37, H 6.67.

**X-ray structure determination of compounds 4a, 17, 25b, and 39**: Single crystals of **4a** were grown from a saturated solution in pentane at −60 °C and those of **17**, **25b**, and **39** by diffusion of diethyl ether into a saturated solution in acetone at room temperature. Crystal data collection parameters are summarized in Table 1. Intensity data were corrected for Lorentz

Table 1. Crystal stucture data of compounds **4a**, **17**, **25b**, and **39**.

| | **4a** | **17** | **25b** | **39** |
|---|---|---|---|---|
| formula | $C_{56}H_{92}Cl_2P_4Rh_2$ | $C_{32}H_{54}ClP_2Rh$ | $C_{32}H_{34}BF_4P_2Rh$ | $C_{24}H_{39}BF_4OPRh$ |
| molecular mass | 1165.90 | 639.05 | 690.41 | 564.24 |
| crystal size [mm] | 0.21 × 0.17 × 0.15 | 0.20 × 0.20 × 0.10 | 0.20 × 0.18 × 0.12 | 0.51 × 0.50 × 0.31 |
| crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ (no. 14) | $P2_1/n$ (no. 14) | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) |
| $a$ [Å] | 10.6377(8) | 8.8783(18) | 11.5556(17) | 10.3339(5) |
| $b$ [Å] | 12.2973(9) | 17.190(3) | 8.8539(8) | 14.3202(7) |
| $c$ [Å] | 21.8499(17) | 21.126(4) | 32.466(5) | 17.1647(9) |
| $\beta$ [°] | 93.8120(10) | 98.92(3) | 95.290(17) | 96.4800(10) |
| $V$ [Å³] | 2852.0(4) | 3185.2(11) | 3307.5(7) | 2523.9(2) |
| $Z$ | 2 | 4 | 4 | 4 |
| $\rho_{calcd}$ [g cm$^{-3}$] | 1.358 | 1.333 | 1.386 | 1.485 |
| diffractometer | Bruker Smart Apex | Stoe IPDS | Stoe IPDS | Bruker Smart Apex |
| radiation (graphite-monochromated) | $Mo_{K\alpha}$ (0.71073 Å) | $Mo_{K\alpha}$ (0.71073 Å) | $Mo_{K\alpha}$ (0.71073 Å) | $Mo_{K\alpha}$ (0.71073 Å) |
| $T$ [K] | 173(2) | 173(2) | 173(2) | 173(2) |
| $\nu$ [mm$^{-1}$] | 0.819 | 0.740 | 0.656 | 0.784 |
| scan method | $\omega$ scans | $\varphi$ scans | $\varphi$ scans | $\omega$ scans |
| $2\theta$(max) [°] | 52.74 | 52.74 | 50.00 | 56.18 |
| total reflections | 45142 | 32867 | 23494 | 41750 |
| unique reflections | 5837 | 6512 | 5759 | 5874 |
| observed reflections [$I > 2\sigma(I)$] | 5631 | 4075 | 3980 | 5766 |
| parameters refined | 297 | 340 | 373 | 295 |
| $R_1$ | 0.0457 | 0.0450 | 0.0277 | 0.0249 |
| $wR_2$ | 0.1032 | 0.1026 | 0.0560 | 0.0640 |
| GOF | 1.310 | 0.887 | 0.856 | 1.087 |
| reflection/parameter ratio | 19.65 | 19.15 | 15.4 | 19.91 |
| residual electron density [eÅ$^{-3}$] | +1.193/−0.398 | +0.897/−1.259 | +0.460/−0.572 | +0.514/−0.502 |

and polarization effects and a semiempirical absorption correction was applied for **4a** and **39**. The structures of **17** and **25b** were solved by direct methods and those of **4a** and **39** by the Patterson method (SHELXS-97).[31] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by the full-matrix least-squares method (SHELX-97).[32] The position of all hydrogen atoms were calculated according to ideal geometry (distance C–H = 0.95 Å) and refined by using the riding method; they were used only in structure factor calculation. The asymmetric unit of **4a** contains only half a molecule.[33]

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