Selective C-Cl Bond Oxidative Addition of Chloroarenes to a POP-Rhodium Complex

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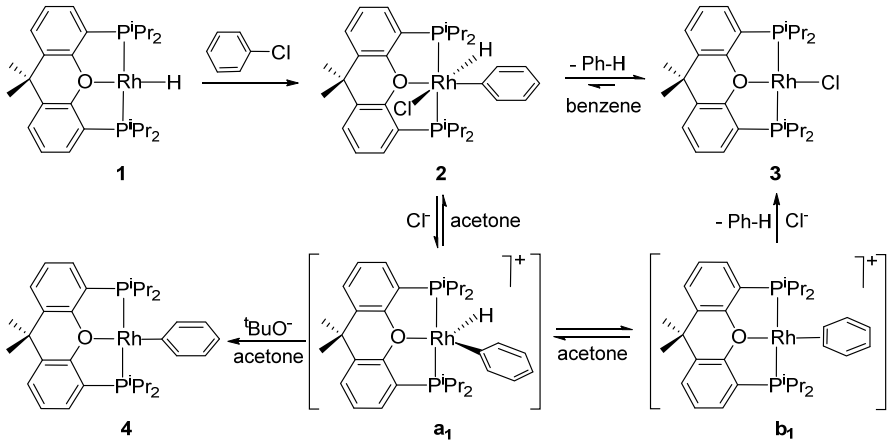
ABSTRACT: The C-Cl bond *cis*-oxidative addition of twelve chloroarenes including chlorobenzene, chlorotoluenes, chlorofluorobenzenes, and di- and trichlorobenzenes to RhH{xant(P^iPr_2)$_2$} (**1**; xant(P^iPr_2)$_2$ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene) and the ability of the resulting rhodium(III) species to undergo reductive elimination reactions are reported. Complex **1** reacts with chlorobenzene to give RhHCl(C_6H_5){xant(P^iPr_2)$_2$} (**2**), which eliminates benzene to afford RhCl{xant(P^iPr_2)$_2$} (**3**). On the other hand, in the presence of potassium *tert*-butoxide (KO^tBu), it undergoes dehydrodechlorination to yield Rh(C_6H_5){xant(P^iPr_2)$_2$} (**4**). The reactions of **1** with 3- and 4-chlorotoluene lead to RhHCl(C_6H_4-3-Me){xant(P^iPr_2)$_2$} (**5**) and RhHCl(C_6H_4-4-Me){xant(P^iPr_2)$_2$} (**6**), respectively. Treatment of the acetone solutions of both compounds with KO^tBu also produces their dehydrodechlorination to give Rh(C_6H_4-3-Me){xant(P^iPr_2)$_2$} (**7**) and Rh(C_6H_4-4-Me){xant(P^iPr_2)$_2$} (**8**). Chlorofluorobenzenes undergo both C-Cl oxidative addition and C-H bond activation in a competitive manner. The amount of the C-H activation product increases as fluorine and chlorine are separated. Complex **1** reacts with *ortho*-chlorofluorobenzene to afford the C-Cl oxidative addition product RhHCl(C_6H_4-2-F){xant(P^iPr_2)$_2$} (**9**). The reaction of **1** with *meta*-chlorofluorobenzene leads to RhHCl(C_6H_4-3-F){xant(P^iPr_2)$_2$} (**10**; 91%) and the C-H bond activation product Rh(C_6H_3-2-Cl-6-F){xant(P^iPr_2)$_2$} (**12**; 9%), whereas *para*-chlorofluorobenzene gives a mixture of RhHCl(C_6H_4-4-F){xant(P^iPr_2)$_2$} (**13**; 61%) and Rh(C_6H_3-3-Cl-6-F){xant(P^iPr_2)$_2$} (**15**; 39%). The addition of KO^tBu to the acetone solutions of **9**, **10** and **13** produces the HCl abstraction and the formation of Rh(C_6H_4-2-F){xant(P^iPr_2)$_2$} (**16**), Rh(C_6H_4-3-F){xant(P^iPr_2)$_2$} (**17**), and Rh(C_6H_4-4-F){xant(P^iPr_2)$_2$} (**18**). In contrast to *ortho*-chlorofluorobenzene, 1,2-dichlorobenzene reacts with **1** to give RhHCl(C_6H_4-2-Cl){xant(P^iPr_2)$_2$} (**19**; 32%), Rh(C_6H_4-2-Cl){xant(P^iPr_2)$_2$} (**20**; 51%) and Rh(C_6H_3-2,3-Cl_2){xant(P^iPr_2)$_2$} (**22**; 17%). The reactions of **1** with 1,3- and 1,4-dichlorobenzene lead to the respective C-Cl bond oxidative addition products RhHCl(C_6H_4-3-Cl){xant(P^iPr_2)$_2$} (**23**) and RhHCl(C_6H_4-4-Cl){xant(P^iPr_2)$_2$} (**24**), which afford Rh(C_6H_4-3-Cl){xant(P^iPr_2)$_2$} (**25**) and Rh(C_6H_4-4-Cl){xant(P^iPr_2)$_2$} (**26**) by dehydrodechlorination with KO^tBu in acetone. Treatment of **1** with 1,2,3-, 1,2,4- and 1,3,5-trichlorobenzene leads to RhHCl(C_6H_3-2,3-Cl_2){xant(P^iPr_2)$_2$} (**27**), RhHCl(C_6H_3-3,4-Cl_2){xant(P^iPr_2)$_2$} (**28**), and RhHCl(C_6H_3-3,5-Cl_2){xant(P^iPr_2)$_2$} (**29**). The addition of KO^tBu to acetone solutions of **27**-**29** affords **22**, Rh(C_6H_3-3,4-Cl_2){xant(P^iPr_2)$_2$} (**30**) and Rh(C_6H_3-3,5-Cl_2){xant(P^iPr_2)$_2$} (**31**).

INTRODUCTION

Organometallic-catalyzed cross-coupling reactions are among the industrial technologies of the highest significance.[1] The C-X bond oxidative addition of an organic halide to the coordinatively unsaturated metal center of a transition metal complex is the essential step of the process, which further determines the reaction rate. In spite of that chlorides are generally less reactive than bromides, iodides and triflates, they are the most useful class of substrates because of their lower cost and wider diversity of available compounds.[2] Palladium(0) complexes have been until now the most powerful tools to perform these reactions.[3] However, in the last years, notable examples have appeared where rhodium catalysts enable C-C coupling of aryl halides.[4] Rhodium catalysts have also shown to play a notable role in the dehalogenation of chloroarenes;[5] a high-priority target from an environmental point of view, since the accumulation of these pollutants is a serious health hazard.

In the search for new catalysts of these relevant reactions, and to gain insight into the mechanism, the oxidative addition of aryl halides to rhodium complexes is waking a great interest in recent years. Grushin and co-workers have reported that the fluoride congener of the Wilkinson's catalyst RhF(PPh_3)$_3$ easily activates the C-Cl bond of Ar-Cl (Ar = Ph, *p*-tolyl) to produce *trans*-RhCl(PPh_2F)(PPh_3)$_2$ and Ar-Ph via *cis*-RhCl(PPh_2F)(PPh_3)$_2$.[6] Weller and co-workers have observed that the highly unsaturated cation $[Rh(P^iBu_3)_2S_x]^+$ (S = solvent) coordinates PhX to give η^6-arene intermediates, which evolve into the dinuclear derivatives $[Rh(\mu\text{-}X)Ph(P^iBu_3)_2]^{2+}$ (X = Cl, Br).[7] The neutral species Rh{κ^2-*N*,*N*-[ArNCMeCHCMeNAr]}S_x similarly gives [Rh(μ-X)Ph{κ^2-*N*,*N*-[ArNCMeCHCMeNAr]}]$_2$ (X = Cl, Br; Ar = 2,6-Me_2CH_3),[8] whereas the known cation $[Rh(PPh_3)_2(acetone)_2]^+$ promotes the chelate-assisted C-X bond activation (X = Cl, Br, I) of 2-(2-halophenyl)pyridines and 10-halobenzo[*h*]quinolines to yield 16-valence electrons five-coordinate cationic rhodium(III) monohalide compounds.[9] Recently, the C-Cl bond cleavage of *para*-substituted chlorobenzenes has been also achieved with RhCl(ttp) (ttp = tetrakis-4-tolylporphyrin) through a metaloradical *ipso*-substitution mechanism.[10]

Pincer ligands offer thermal stability and the prevention of undesired ligand exchange and redistribution,[11] which has allowed the development of particularly relevant catalytic reactions in recent years.[12] Although these properties are notable advantages from the point of view of the cross-coupling and dehalogenation catalysis, the fascination by the pincer systems



Scheme 1. Reaction of Complex 1 with Chlorobenzene.

has scarcely reached the oxidative addition of aryl halides to rhodium. Nishiyama and co-workers have reported the oxidative addition of chlorobenzene, *p*-chlorotoluene and 2-chloropyridine to Rh(Phebox) (Phebox = bis(oxazolynyl)phenyl),[13] whereas Ozerov and co-workers have studied the oxidative addition of a variety of *meta*- and *para*-substituted aryl halides to Rh(PNP) (PNP = bis(2-(diisopropylphosphino)-4-methylphenyl)amino). In agreement with the Nishiyama's results, the Ozerov's group has generally obtained five-coordinate complexes of formula Rh(Ar)(X)(PNP) (X = Cl, Br, I). However, substrates containing a *p*-NO_2 or *p*-CO_2Me group initially lead to C-H bond activation products. In spite that these compounds are stabilized by coordination of NO_2 or CO_2Me, they are converted into the aryl halide oxidative addition products upon thermolysis. Hammett studies suggest an earlier transition state in a concerted process.[14] DFT calculations to analyze competitive C-H versus C-Cl oxidative addition of chlorobenzene to the model complex Rh(P'N'P') (P'N'P' = bis(*Z*-2-(dimethylphosphino)vinyl)amino) show that the C-Cl and C-H oxidative additions are kinetically competitive. However, the C-Cl oxidative addition product is thermodynamically preferred over the most stable C-H oxidative addition product.[15]

Neutral POP diphosphines are a class of pincers with hemilabile properties,[16] which are less rigid than the anionic NCN and PNP ligands used by Nishiyama and Ozerov. As a consequence of this flexibility, rhodium complexes containing these ligands are playing a significant role in catalysis. Thus, some of them have shown to promote a wide range of interesting organic reactions,[17] including decyanative borylation,[18] as well as the dehydrocoupling and dehydropolymerization of amine-boranes.[19] The square-planar monohydride RhH{xant(P^iPr_2)$_2$} (**1**; xant(P^iPr_2)$_2$ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene) is a notable example of POP-rhodium complex,[20] which promotes the catalytic formation of B-C bonds[21] and activates the Si-H bond of silanes,[22] the B-H bond of boranes, and a C-H bond of arenes.[21] We now show that it is also able to add a C-Cl bond of aryl chlorides. This paper reports the oxidative addition of chlorobenzene, chlorotoluenes, chlorofluorobenzenes, and di- and trichlorobenzenes to **1**. The influence of the substituents of the arene on the position of the activated bond is rationalized.

RESULTS AND DISCUSSION

Chlorobenzene. It has been previously shown that complex **1** promotes the *ortho*-CH bond activation of fluorobenzene to afford the square-planar aryl derivative Rh(C_6H_4-2-F){xant(P^iPr_2)$_2$} and molecular hydrogen.[21] In contrast to fluorobenzene, chlorobenzene undergoes a selective carbon-halide bond activation reaction. Thus, treatment of pentane solutions of **1** with 2.0 equiv of the aryl-halide, at room temperature, for 24 h leads to the rhodium(III) derivative RhHCl(C_6H_5){xant(P^iPr_2)$_2$} (**2**), as a result of the *cis*-oxidative addition of the C-Cl bond of chlorobenzene to **1** (Scheme 1).

Complex **2** was isolated as a beige solid in 60% yield and characterized by X-ray diffraction analysis. The structure (Figure 1) proves the C-Cl bond activation. As expected for a pincer coordination of the diphosphine, the Rh(POP) skeleton is T-shaped with the rhodium situated in the common vertex and P(1)-Rh-P(2), P(1)-Rh-O(1), and P(2)-Rh-O(1) angles of 159.19(3)º, 82.23(6)º, and 83.10(6)º, respectively. So, the coordination geometry around the metal center can be rationalized as the typical rhodium(III) octahedron with the phenyl *trans* disposed to the oxygen atom of the diphosphine (C(1)-Rh-O(1) = 173.94(12)º) and the hydride and chloride ligands also mutually *trans* disposed (H(1)-Rh-Cl(1) = 178.0(12)º). This ligand disposition is consistent with a concerted cleavage of the C-Cl bond, which occurs along the O-Rh-H axis of **1** with the electron rich chloride disposed above the electron rich oxygen atom of the diphosphine.[23] So, the reason of this preference appears to be steric. The Rh-C(1) bond length of 2.007(4) Å compares well with rhodium(III)-aryl distances previously reported.[24]

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **2**, in benzene-d_6, at room temperature are consistent with the structure shown in Figure 1. According to the presence of the hydride ligand, the ^{1}H NMR spectrum contains a double ($^1J_{H\text{-}Rh}$ = 25.5 Hz) triplet ($^2J_{H\text{-}P}$ = 12.8 Hz) at -15.66 ppm. In the ^{13}C{^{1}H} NMR spectrum, the most noticeable resonance is that corresponding to the metalated carbon atom of the phenyl group, which appears at 145.1 ppm and is observed as a double triplet with C-Rh and C-P coupling constants of 35.4 and 9.9 Hz, respectively. Both ^{1}H and ^{13}C{^{1}H} NMR spectra show three CH-resonances due to the phenyl ligand, suggesting that this group rotates around the Rh-Ph bond, in solution, at room temperature. The activation energy for the process, measured in acetone, is 12 kcal·mol^{-1}. The ^{31}P{^{1}H} NMR spectrum contains at 40.6 ppm a doublet with a value for the P-Rh coupling constant of 114.5 Hz, which is typical for rhodium(III).

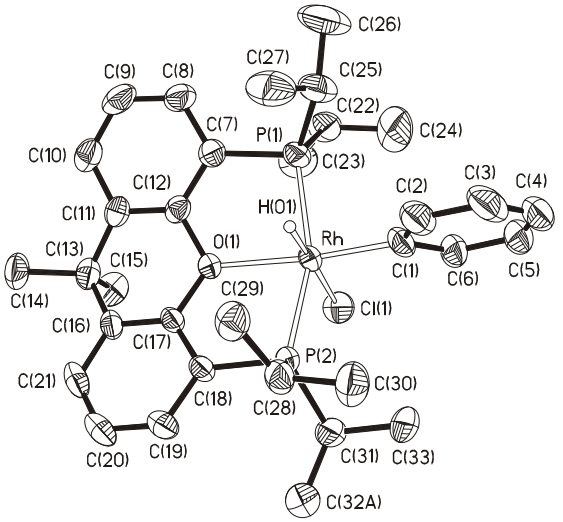
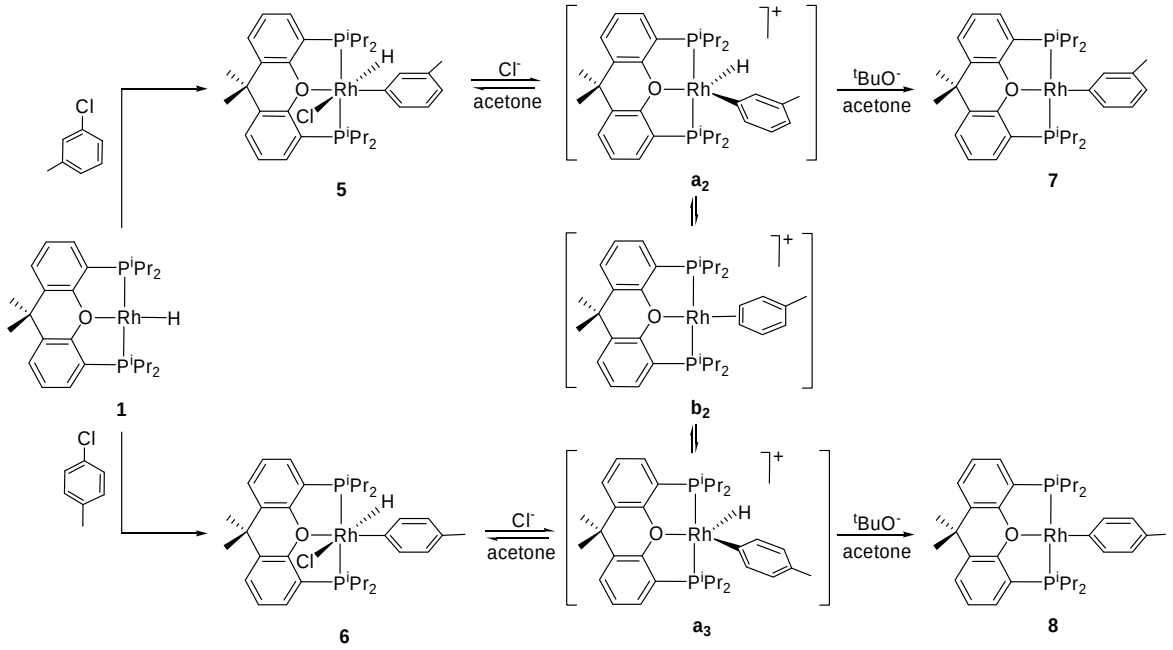


Figure 1. ORTEP diagram of complex **2** (50% probability ellipsoids). Hydrogen atoms (except the hydride) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh-P(1) = 2.2752(10), Rh-P(2) = 2.2963(10), Rh-Cl(1) = 2.5130(11), Rh-O(1) = 2.246(2), Rh-C(1) = 2.007(4); P(1)-Rh-P(2) = 159.19(3), P(1)-Rh-O(1) = 82.23(6), P(2)-Rh-O(1) = 83.10(6), P(1)-Rh-Cl(1) = 101.54(4), P(2)-Rh-Cl(1) = 91.99(4), P(1)-Rh-C(1) = 93.33(10), P(2)-Rh-C(1) = 100.08(11), C(1)-Rh-Cl(1) = 99.27(12), C(1)-Rh-O(1) = 173.94(12), H(1)-Rh-Cl(1) = 178.0(12).

Complex **2** is unstable with regard to the reductive elimination of benzene (Scheme 1). In acetone, it quantitatively affords the rhodium(I) chloride derivative $RhCl\{xant(P^iPr_2)_2\}$ (**3**) and benzene, after 7 days, at 40 ºC. In agreement with this, the benzene solutions of **3** only contain about 13% of **2**, after 12 days, at room temperature. It should be however mentioned that complex **2** can be kept in benzene solution, under argon, for long time. This suggests that the activation energy for the reductive elimination of the hydrocarbon from **2** is high and depends upon the solvent, being favored in polar media. It is well known that unsaturated metal centers favor reductive elimination reactions.[25] So, the polar solvent seems to promote the chloride dissociation from **2** to afford the unsaturated rhodium(III)-hydride-aryl cation $[RhH(C_6H_5)\{xant(P^iPr_2)_2\}]^+$ (**a_1**). The subsequent reductive elimination of benzene from **a_1** would give the η^2-benzene intermediate $[Rh(\eta^2\text{-}C_6H_6)\{xant(P^iPr_2)_2\}]^+$ (**b_1**); in this context it should be noted that this type of species are the key intermediates for the C-H bond activation of arenes.[26] Thus, the displacement of the coordinated arene by chloride could generate **3**. In support of the transitory formation of **a_1**, we have also observed that the addition of potassium *tert*-butoxide (KO^tBu) to the acetone solutions of **2** rapidly leads to the rhodium(I)-phenyl derivative $Rh(C_6H_5)\{xant(P^iPr_2)_2\}$ (**4**), as a result of the deprotonation of **a_1**. It should be noted that the pK_a of a cationic hydride is lower than that of a neutral hydride. An additional evidence of the formation of **a_1** is that the addition of three equivalents of $(N^nBu_4)Br$ to an acetone solution of **2** affords the bromide counterpart $RhHBr(C_6H_5)\{xant(P^iPr_2)_2\}$ (^{1}H: $\delta_{hydride}$ –15.12, $^2J_{H\text{-}P}$ = 12.6 Hz, $^1J_{H\text{-}Rh}$ = 27.7 Hz. $^{31}P\{^1H\}$: δ 39.7, $^1J_{P\text{-}Rh}$ = 115.1, which also eliminates benzene to afford the square-planar derivative $RhBr\{xant(P^iPr_2)_2\}$ ($^{31}P\{^1H\}$: δ 38.9, $^1J_{P\text{-}Rh}$ = 138.4).

Chlorotoluenes. Similarly to chlorobenzene, 3- and 4-chlorotoluene undergo selective carbon-halide bond activation. Reactions of **1** with these substrates lead to the respective rhodium(III) complexes $RhHCl(C_6H_4\text{-}3\text{-}Me)\{xant(P^iPr_2)_2\}$ (**5**) and $RhHCl(C_6H_4\text{-}4\text{-}Me)\{xant(P^iPr_2)_2\}$(**6**), resulting from the *cis*-oxidative addition of the C-Cl bond of the aryl-halides (Scheme 2). Complexes **5** and **6** were isolated as beige solids in 50-60% yields. Their ^{1}H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra, in benzene-d_6, at room temperature agree well with those of **1**. The ^{1}H NMR spectra show the hydride resonance at -15.6 ($^1J_{H\text{-}Rh} \approx 26$ Hz, $^2J_{H\text{-}P} \approx 13$ Hz) ppm whereas, in the $^{13}C\{^1H\}$ NMR spectra, the signal corresponding to the metalated aryl carbon atom is observed at 144.5 ppm for **5** and 139.9 ppm for **6** with C-Rh and C-P coupling constants of about 35 and 10 Hz, respectively. Like in **2**, the tolyl ligands rotate around the Rh-tolyl bond overcoming an activation energy close to 12 kcal·mol^{-1}. The $^{31}P\{^1H\}$ NMR spectra contain the expected doublet ($^1J_{P\text{-}Rh} \approx 117$ Hz) at 40 ppm.

The reductive elimination of toluene from both **5** and **6** is not observed in benzene or acetone. However, complexes **5** and **6** also undergo dehydrodechlorination, in acetone, at room temperature. Thus, similarly to **2**, the addition of KO^tBu to their acetone solutions leads to the respective square planar derivatives $Rh(C_6H_4\text{-}3\text{-}Me)\{xant(P^iPr_2)_2\}$ (**7**) and $Rh(C_6H_4\text{-}4\text{-}Me)\{xant(P^iPr_2)_2\}$ (**8**). In the absence of the base, both compounds afford the same mixture, after one day, at room temperature. Its composition is 43% of **5**, 20% of **6**, 15% of **7** and 22% of **8**. This fact, which can be rationalized according to Scheme 2, is consistent with the transitory formation of the five-coordinate cations $[RhH(C_6H_4\text{-}3\text{-}Me)\{xant(P^iPr_2)_2\}]^+$ (**a_2**) and $[RhH(C_6H_4\text{-}4\text{-}Me)\{xant(P^iPr_2)_2\}]^+$ (**a_3**) in equilibrium with the η^2-tolyl intermediate $[Rh(\eta^2\text{-}C_6H_5Me)\{xant(P^iPr_2)_2\}]^+$ (**b_2**). The higher coordination power of toluene with regard to benzene could explain why in this case the chloro derivative **3** is not observed and why the reductive elimination of HCl is favored with regard to the reductive elimination of the arene, in opposite to **2**. In favor of this proposal it should be mentioned that complex **5** can be kept in benzene, under argon, at room temperature, for at least 48 h, without observing aryl exchange with the solvent. The square-planar tolyl compounds **7** and **8** do not isomerize between them, in contrast to that observed for their rhodium(III) precursors.

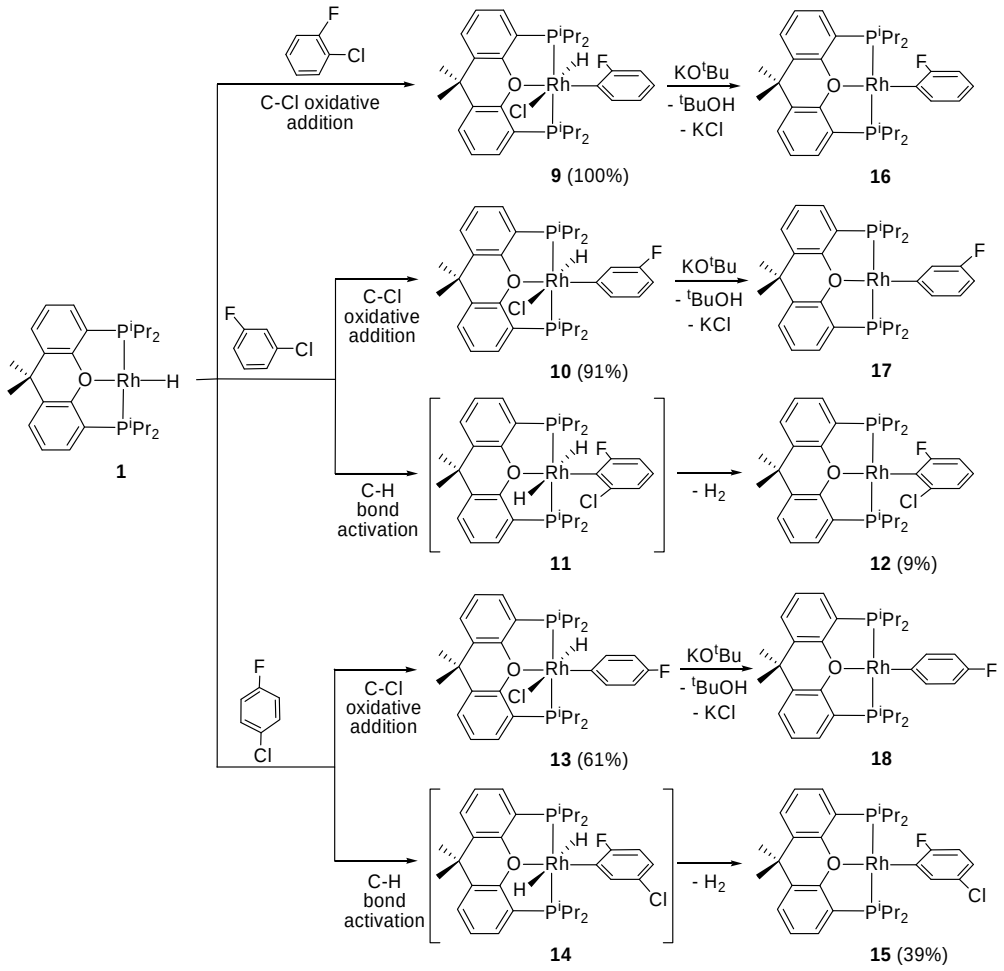


Scheme 2. Reactions of Complex 1 with 3- and 4-Chlorotoluene.

Chlorofluorobenzenes. In contrast to chlorobenzene and chlorotoluenes, chlorofluorobenzenes undergo both C-Cl oxidative addition and C-H bond activation in a competitive manner, although the C-Cl oxidative addition product is always the major one. The amount of the minor C-H bond activation product is sensitive to the position of the fluorine atom in the aromatic ring, increasing as is away from the chlorine atom (Scheme 3).

Complex **1** reacts with *ortho*-chlorofluorobenzene to selectively afford the C-Cl oxidative addition product RhHCl(C_6H_4-2-F){xant(P^{i}Pr$_2$)$_2$} (**9**). The reaction of **1** with *meta*-chlorofluorobenzene leads to a mixture of RhHCl(C_6H_4-3-F){xant(P^{i}Pr$_2$)$_2$} (**10**; 91%) and the C-H bond activation product RhH$_2$(C_6H_3-2-Cl-6-F){xant(P^{i}Pr$_2$)$_2$} (**11**), which is unstable and rapidly loses molecular hydrogen to generate the square-planar rhodium(I) derivative[21] Rh(C_6H_3-2-Cl-6-F){xant(P^{i}Pr$_2$)$_2$} (**12**; 9%), whereas *para*-chlorofluorobenzene gives a mixture of RhHCl(C_6H_4-4-F){xant(P^{i}Pr$_2$)$_2$} (**13**; 61%) and RhH$_2$(C_6H_3-3-Cl-6-F){xant(P^{i}Pr$_2$)$_2$} (**14**). Similarly to **11**, complex **14** loses molecular hydrogen to afford Rh(C_6H_3-3-Cl-6-F){xant(P^{i}Pr$_2$)$_2$} (**15**; 39%). The selectivity observed for the C-H bond activation is consistent with the expected increase of the M-C bond energy with the *ortho*-fluorine substitution.[27] This effect, which has been explained in terms of an increase of the ionic component of the M-C bond through inductive effect of the *ortho*-halide,[28] also seems to operate for the chlorine substituent as is proven by the formation of **12**, although it is weaker.

The difference in solubility between the rhodium(III) and the rhodium(I) species, in pentane, allowed us the extraction of the latter from the mixture. As a consequence, the rhodium(III) complexes **9**, **10** and **13** were isolated in 40-82% yield, as analytically pure beige solids. Their ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra, in benzene-d_6, at room temperature are consistent with those of **2**, **5**, and **6**. In the ^{1}H NMR spectra, the hydride signal appears between -14.7 and -15.7 ppm. For **10** and **13**, it is observed as a double triplet with H-Rh and H-P coupling constants close to 26 and 13 Hz, respectively, whereas the hydride resonance of **9** shows an additional H-F coupling constant of 6.2 Hz, which suggests an intramolecular H···F interaction. In agreement with this, rotation of the aryl ligand of **9** around the Rh-aryl bond is not observed, at room temperature, whereas the coordinated aryl groups of **10** and **13** rotate around the respective Rh-aryl bonds overcoming an activation barrier of 12 kcal·mol^{-1}, like the aryl ligands of **2**, **5**, and **6**. In the ^{13}C{^{1}H} NMR spectra, the resonance due to the metalated aryl carbon atom appears between 147 and 157 ppm. The ^{31}P{^{1}H} NMR spectra contain a doublet ($^1J_{P\text{-}Rh}$ = 111-114 Hz) between 40 and 44 ppm. The formation of the square-planar rhodium(I)-aryl complexes **12** and **15** was mainly inferred from the ^{31}P{^{1}H} and ^{1}H NMR spectra of the mixtures. According to the *ortho*-disposition of the fluorine and rhodium atoms in both compounds, the ^{31}P{^{1}H} NMR spectra show at about 40 ppm the characteristic double doublet due to the spin coupling between P and Rh nuclei ($^1J_{P\text{-}Rh} \approx$ 164 Hz), and between the P and F nuclei ($^3J_{P\text{-}F}$ = 4 Hz). The most noticeable feature of the ^{1}H NMR spectrum of **12** is a double doublet of doublets with a H-F coupling constant of 11.3 Hz and H-H coupling constants of 7.4 and 1.8 Hz, at 8.42 ppm, which supports the presence of a hydrogen atom *ortho* disposed to the fluorine substituent, in the aromatic ring. In the ^{1}H NMR spectrum of **15**, a double triplet with H-P and H-Rh coupling constants of 3 Hz, at 7.78 ppm, confirms the *ortho* disposition of an aromatic hydrogen atom to the metal center in this compound.



Scheme 3. Reactions of Complex 1 with Chlorofluorobenzenes.

The rhodium(III)-fluorophenyl complexes **9**, **10** and **13** also undergo dehydrochlorination in acetone. Similarly to **2**, **5** and **6**, the addition of KO^{t}Bu to the acetone solutions of these compounds produces the elimination of HCl and the formation of the rhodium(I) derivatives Rh(C_6H_4-2-F){xant(P^iPr_2)$_2$} (**16**), Rh(C_6H_4-3-F){xant(P^iPr_2)$_2$} (**17**), and Rh(C_6H_4-4-F){xant(P^iPr_2)$_2$} (**18**), which were isolated as orange solids in about 90% yield, according to Scheme 3. Complex **17** was characterized by X-ray diffraction analysis. Figure 2 shows a drawing of the molecule. The coordination geometry around the rhodium atom is almost square-planar with the diphosphine coordinated in *mer*-fashion (P(1)-Rh-P(2) = 163.24(5)^o, P(1)-Rh-O(1) = 82.45(8)^o, P(2)-Rh-O(1) = 82.39(8)^o) and the aryl group *trans* disposed to the oxygen atom of the diphosphine (C(1)-Rh-O(1) = 176.93(13)^o). The greatest deviation from the best plane through Rh, C(1), P(1), O(1) and P(2) atoms is 0.091(1) Å and involves to P(1). The Rh-C(1) bond length of 1.987(5) Å is statistically identical with the Rh-aryl distance found in the previously reported complex **16** (1.994(4) Å).[21] The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of **17** and **18**, in benzene-d_6, at room temperature agree well with those of **16** and are consistent with the structure shown in Figure 2. In the $^{13}C\{^1H\}$ NMR spectra, the resonance due to the metalated aryl carbon atom is observed at 167.0 ppm for **17** and 153.3 ppm for **18**. The $^{31}P\{^1H\}$ NMR spectra contain the expected doublet ($^1J_{P\text{-}Rh}$ = 174 Hz) at about 37 ppm.

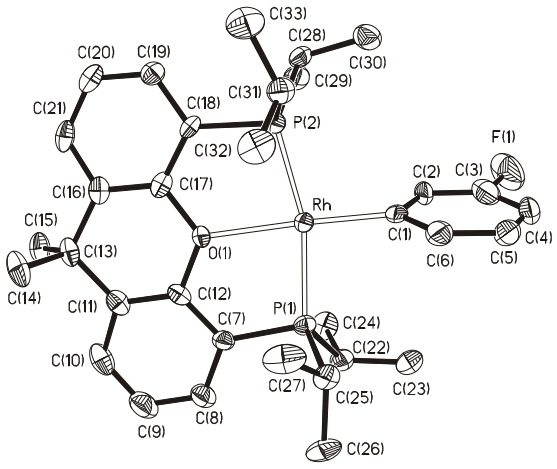
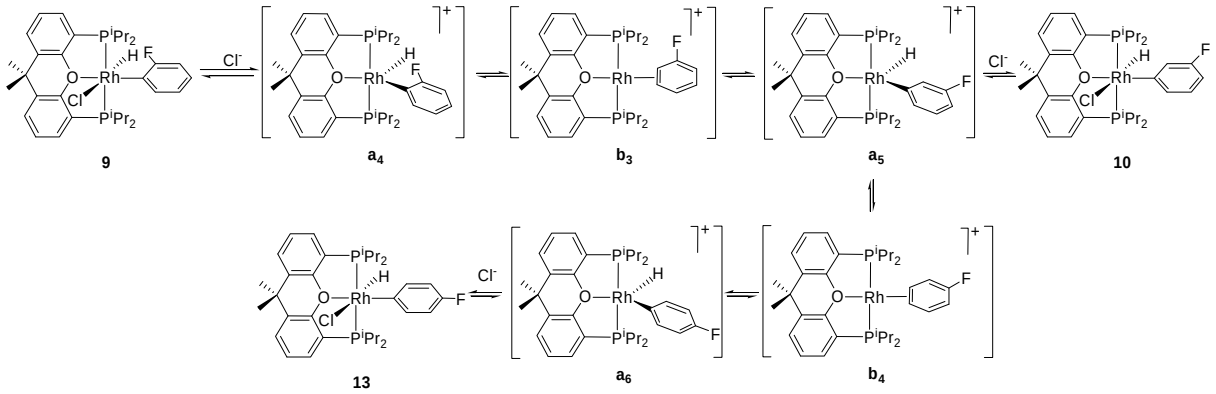


Figure 2. ORTEP diagram of complex **17** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh-P(1) = 2.2393(11), Rh-P(2) = 2.2429(11), Rh-O(1) = 2.219(3), Rh-C(1) = 1.987(5); P(1)-Rh-P(2) = 163.24(5), P(1)-Rh-O(1) = 82.45(8), P(2)-Rh-O(1) = 82.39(8), P(1)-Rh-C(1) = 94.77(12), P(2)-Rh-C(1) = 100.53(15), C(1)-Rh-O(1) = 176.93(13).



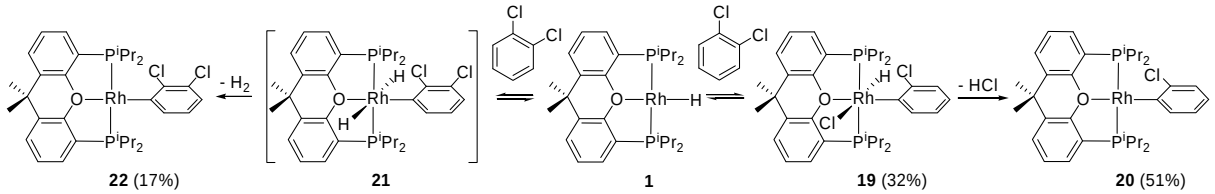
Scheme 4. Isomerization between Complexes 9, 10, and 13.

The rhodium(I) complexes **16**-**18** are stable in acetone-d_6. Thus, their solutions can be kept by long time, at room temperature, under argon. However, in the absence of base, the rhodium(III) precursors **9**, **10**, and **13** afford complex mixtures of rhodium(III) and rhodium(I) species, resulting from reactions of isomerization (Scheme 4), HCl reductive elimination, and sequential chlorofluorobenzene reductive elimination – CH bond activation. The instability of the rhodium(III) compounds increases as the fluorine substituent of the phenyl ligand is away from the rhodium atom. After 7 days, the 2-fluorophenyl complex **9** isomerizes into the 3-fluorophenyl derivative **10** (16%) via the transitory cations $[RhH(C_6H_4\text{-}2\text{-}F)\{xant(P^iPr_2)_2\}]^+$ (**a**$_4$), $[Rh(\eta^2\text{-}C_6H_5F)\{xant(P^iPr_2)_2\}]^+$ (**b**$_3$), and $[RhH(C_6H_4\text{-}3\text{-}F)\{xant(P^iPr_2)_2\}]^+$ (**a**$_5$), and eliminates HCl to give **16** (27%). After the same time, complex **10** gives its isomer **9** (8%), the dehydrodechlorination products **16** (27%) and **17** (17%), and the C-H bond activation product **12** (14%), whereas the 4-fluorophenyl compound **13** evolves into **10** (7%), **16** (21%), **17** (22%) and the C-H bond activation product **15** (43%). Although the transformations of **10** and **13** into **12** and **15** are relevant processes, according to the percentages above mentioned, this does not mean that the C-H bond activation of the chlorofluorobenzenes is a competitive process with the C-Cl bond activation, from a thermodynamically point of view, because the reason for these percentages appears to be the loss of the volatile H_2 molecule.

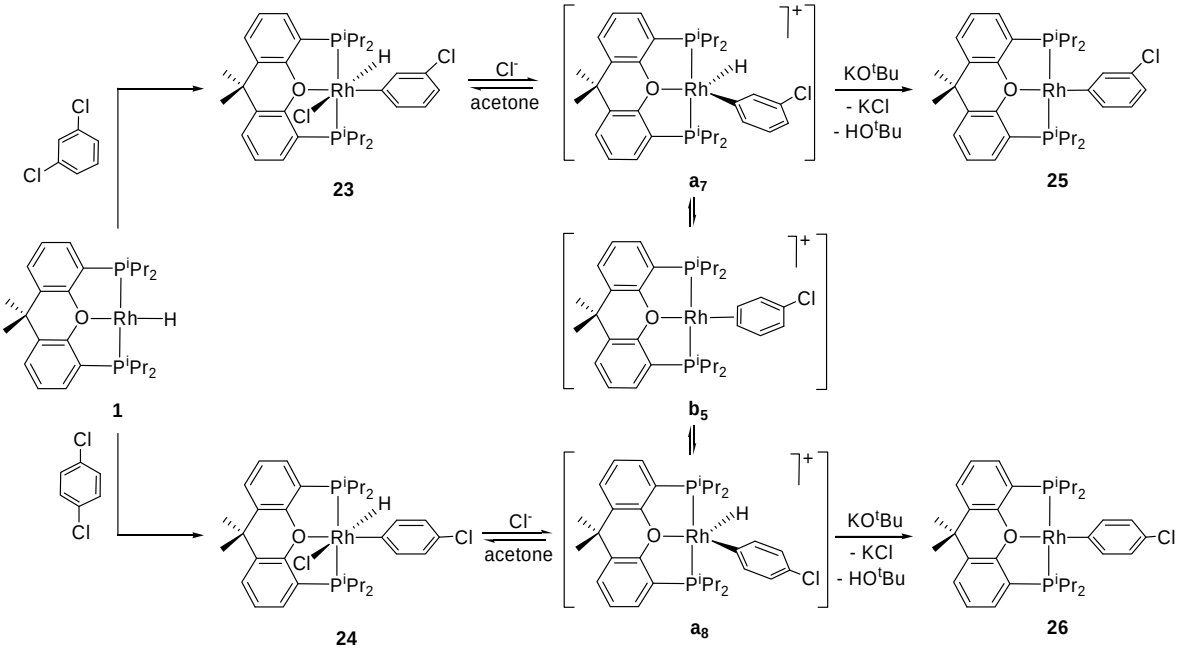
Dichlorobenzenes. The replacement of the fluorine substituent of chlorofluorobenzenes by a chlorine atom has a marked influence on the behavior of the aromatic substrate. In contrast to *ortho*-chlorofluorobenzene, 1,2-dichlorobenzene slowly reacts with **1**, in benzene, at room temperature to give a mixture of the C-Cl oxidative addition product $RhHCl(C_6H_4\text{-}2\text{-}Cl)\{xant(P^iPr_2)_2\}$ (**19**), the rhodium(I) compound $Rh(C_6H_4\text{-}2\text{-}Cl)\{xant(P^iPr_2)_2\}$ (**20**) resulting of the HCl reductive elimination from **19**, and the transitory C-H bond activation dihydride species $RhH_2(C_6H_3\text{-}2,3\text{-}Cl_2)\{xant(P^iPr_2)_2\}$ (**21**), which rapidly loses molecular hydrogen to afford the square-planar complex $Rh(C_6H_3\text{-}2,3\text{-}Cl_2)\{xant(P^iPr_2)_2\}$ (**22**). After 3 days the composition of the **19**:**20**:**22** mixture is 32:51:17 (Scheme 5). In benzene-d_6, at room temperature, characteristic features of **19** are a double ($^1J_{H\text{-}Rh}$ = 22.3 Hz) triplet ($^3J_{H\text{-}P}$ = 12.1 Hz) at -14.19 (RhH) ppm in the ^{1}H NMR spectrum, a double ($^1J_{C\text{-}Rh}$ = 42.3 Hz) triplet ($^3J_{C\text{-}P}$ =12.5 Hz) at 149.0 (RhC) ppm in the $^{13}C\{^1H\}$ NMR spectrum, and a doublet ($^1J_{P\text{-}Rh}$ = 112.7 Hz) at 42.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The presence of **20** in the mixture is mainly supported by a double ($^1J_{C\text{-}Rh}$ = 43.8 Hz) triplet ($^3J_{C\text{-}P}$ =13.0 Hz) at 161.6 (RhC) ppm in the $^{13}C\{^1H\}$ NMR spectrum and a doublet ($^1J_{P\text{-}Rh}$ = 171.9 Hz) at 38.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum. In agreement with **20**, the $^{13}C\{^1H\}$ NMR spectrum of **22** contains a double ($^1J_{C\text{-}Rh}$ = 44.4 Hz) triplet ($^3J_{C\text{-}P}$ =12.7 Hz) at 166.9 (RhC) ppm, whereas the $^{31}P\{^1H\}$ NMR spectrum shows a doublet ($^1J_{P\text{-}Rh}$ = 170.4 Hz) at 38.4 ppm.

Complex **1** reacts with 1,3- and 1,4-dichlorobenzene to selectively give the C-Cl oxidative addition products $RhHCl(C_6H_4\text{-}3\text{-}Cl)\{xant(P^iPr_2)_2\}$ (**23**) and $RhHCl(C_6H_4\text{-}4\text{-}Cl)\{xant(P^iPr_2)_2\}$ (**24**) which were isolated as beige solids in 72% and 75% yield, respectively (Scheme 6). The relative position of the chlorine atoms in the aromatic ring has a marked influence in the reaction rate, increasing as are separated. Thus, while complex **23** is quantitatively generated after 6 h, the quantitative formation of **24** takes place after 4 h. In agreement with **19**, the ^{1}H NMR spectra of these compounds, in benzene-d_6, at room temperature show the hydride resonance as a double ($^1J_{H\text{-}Rh}$ = 26 Hz) triplet ($^3J_{H\text{-}P} \approx$ 13 Hz) at about -15.8 ppm. In the $^{13}C\{^1H\}$ NMR spectra, the RhC-resonance of the aryl ligand is observed as a double ($^1J_{C\text{-}Rh} \approx$ 37 Hz) triplet ($^3J_{C\text{-}P} \approx$ 10 Hz) between 142 and 147 ppm. $^{31}P\{^1H\}$ NMR spectra contain a doublet ($^1J_{P\text{-}Rh} \approx$ 113 Hz) at 41.2 ppm. The chlorophenyl ligands of both compounds rotate around the Rh-aryl bond. Like in the previous cases, in acetone, the activation energy for the rotation is 12 kcal·mol^{-1}.

Complexes **23** and **24** are stable in benzene. However, in acetone, at room temperature they isomerize to reach the same mixture, after 2 days, which has a **23**:**24** molar ratio of 70:30. In the presence of KO^{t}Bu, both compounds rapidly undergo dehydrodechlorination to afford the respective rhodium(I) derivatives $Rh(C_6H_4\text{-}3\text{-}Cl)\{xant(P^iPr_2)_2\}$ (**25**) and $Rh(C_6H_4\text{-}4\text{-}Cl)\{xant(P^iPr_2)_2\}$ (**26**), which were isolated as orange solids in almost quantitative yield. In contrast to their rhodium(III) precursors, they are stable in acetone and do not isomerize. Complex **25** was characterized by X-ray diffraction analysis. Figure 3 shows a drawing of the molecule.



Scheme 5. Reaction of Complex 1 with 1,2-Dichlorobenzene.



Scheme 6. Reactions of Complex 1 with 1,3- and 1,4-Dichlorobenzene.

Like in **17**, the coordination around the metal center is square-planar with the diphosphine *mer* disposed (P(1)-Rh-P(2) = 164.94(3)º, P(1)-Rh-O(1) = 82.86(6)º, P(2)-Rh-O(1) = 82.77(6)º) and the chlorophenyl group *trans* disposed to the oxygen atom (C(1)-Rh-O(1) = 176.31(11)º). In this case, the greatest deviation from the best plane through Rh, C(1), P(1), O(1) and P(2) is 0.051(9) Å and involves to Rh. The Rh-C(1) bond length of 1.975(3) Å is statistically identical with that of **17**. The $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra of **25** and **26**, in benzene-d_6, at room temperature are consistent with Figure 3 and agree well with those of **10**. In the $^{13}C\{^{1}H\}$ NMR spectra, the RhC-resonance of the chlorophenyl ligand is observed as a double ($^{1}J_{C\text{-}Rh} \approx 41$ Hz) triplet ($^{3}J_{C\text{-}P} \approx 15$ Hz) at 166.6 ppm for **25** and at 160.6 ppm for **26**. The $^{31}P\{^{1}H\}$ NMR spectra contain a doublet ($^{1}J_{P\text{-}Rh} \approx 174$ Hz) at about 37 ppm.

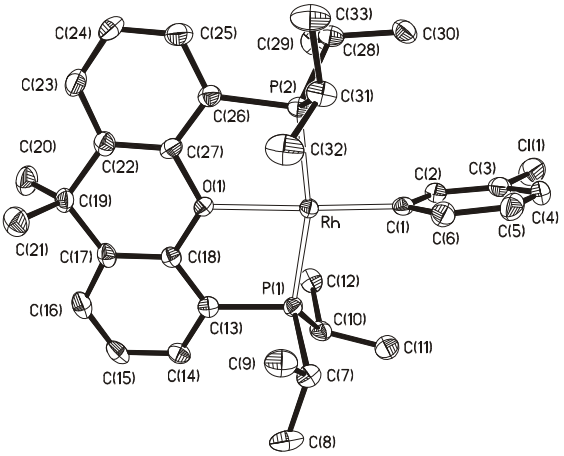
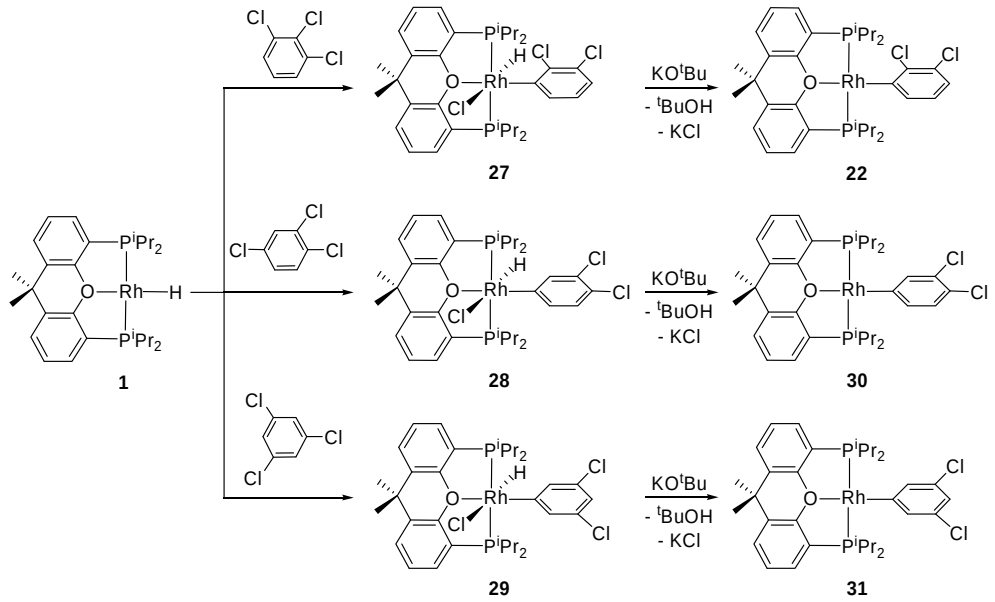


Figure 3. ORTEP diagram of complex **25** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh-P(1) = 2.2430(9), Rh-P(2) = 2.2383(10), Rh-O(1) = 2.209(2), Rh-C(1) = 1.975(3); P(1)-Rh-P(2) = 164.94(3), P(1)-Rh-O(1) = 82.86(6), P(2)-Rh-O(1) = 82.77(6), P(1)-Rh-C(1) = 100.18(10), P(2)-Rh-C(1) = 94.03(10), C(1)-Rh-O(1) = 176.31(11).



Scheme 7. Reactions of Complex 1 with Trichlorobenzenes.

Trichlorobenzenes. Complex **1** also undergoes the oxidative addition of trichlorobenzenes (Scheme 7). In pentane, at room temperature, the reactions show selectivities which appear to be governed by steric reasons. The reaction with 1,2,3-trichlorobenzene slowly gives $RhHCl(C_6H_3\text{-}2,3\text{-}Cl_2)\{xant(P^iPr_2)_2\}$ (**27**), as a result of the addition of one of the external C-Cl bonds to the metal center. Complex **27** eliminates HCl to afford the square-planar rhodium(I) derivative **22**. In acetone, the reductive elimination is quantitative in the presence of KO^{t}Bu. The separation of one of the chlorine substituents from the other two favors the cleavage of the furthest C-Cl bond, which is faster in addition to selective. Thus, complex **1** adds the C-Cl bond at 4-position of 1,2,4-trichlorobenzene to give $RhHCl(C_6H_3\text{-}3,4\text{-}Cl_2)\{xant(P^iPr_2)_2\}$ (**28**). 1,3,5-Trichlorobenzene yields $RhHCl(C_6H_3\text{-}3,5\text{-}Cl_2)\{xant(P^iPr_2)_2\}$ (**29**). Similarly to **27**, the addition of KO^{t}Bu to the acetone solutions of **28** and **29** leads to the corresponding square-planar rhodium(I) derivatives $Rh(C_6H_3\text{-}3,4\text{-}Cl_2)\{xant(P^iPr_2)_2\}$ (**30**) and $Rh(C_6H_3\text{-}3,5\text{-}Cl_2)\{xant(P^iPr_2)_2\}$ (**31**). The rhodium(III) complexes **27**-**29** were isolated as beige solids in 60-86% yield, whereas the rhodium(I) compounds **22**, **30**, and **31** were obtained as red (**22**) or orange solids in almost quantitative yield. In contrast to **23** and **24**, complexes **27** and **28** do not convert between them. This suggests that the replacement of the hydrogen atom at positions 2 or 4 in the chlorophenyl group of **23** by a chlorine increases the activation energy for the reductive elimination of the arene.

Complexes **27** and **29** have been characterized by X-ray diffraction analysis. Figures 4 and 5 show the respective structures. Like in **2**, the coordination geometry around the metal center of both compounds can be described as an octahedron with the diphosphine *mer*-coordinated (P(1)-Rh-P(2) = 161.46(7)^o for **27** and 158.73(5)^o for **29**; P(1)-Rh-O(1) = 82.00(12)^o for **27** and 81.72(9)^o for **29**; and P(2)-Rh-O(1) = 81.96(12)^o for **27** and 82.60(8)^o for **29**), the dichlorophenyl group *trans* disposed to the oxygen atom of the pincer (C(1)-Rh-O(1) = 178.8(3)^o for **27** and 174.30(17)^o for **29**), and the hydride *trans* to the chloride (H(1)-Rh-Cl(1) = 167(2)^o for **27** and 152.3(19)^o for **29**). The rhodium aryl bond lengths (Rh-C(1)) of 2.011(7) Å for **27** and 2.001(5) Å for **29** are statistically identical to that of **2**.

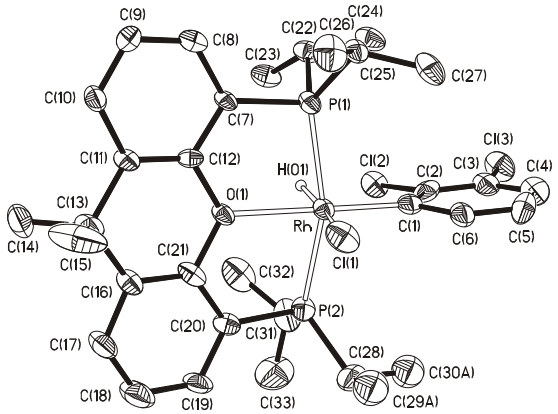


Figure 4. ORTEP diagram of complex **27** (50% probability ellipsoids). Hydrogen atoms (except the hydride) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh-P(1) = 2.301(2), Rh-P(2) = 2.291(2), Rh-Cl(1) = 2.522(2), Rh-O(1) = 2.218(4), Rh-C(1) = 2.011(7); P(1)-Rh-P(2) = 161.46(7), P(1)-Rh-Cl(1) = 91.91(7), P(2)-Rh-Cl(1) = 93.98(7), P(1)-Rh-O(1) = 82.00(12), P(2)-Rh-O(1) = 81.96(12), P(1)-Rh-C(1) = 97.9(2), P(2)-Rh-C(1) = 98.0(2), C(1)-Rh-Cl(1) = 102.5(2), C(1)-Rh-O(1) = 178.8(3), H(1)-Rh-Cl(1) = 167(2).

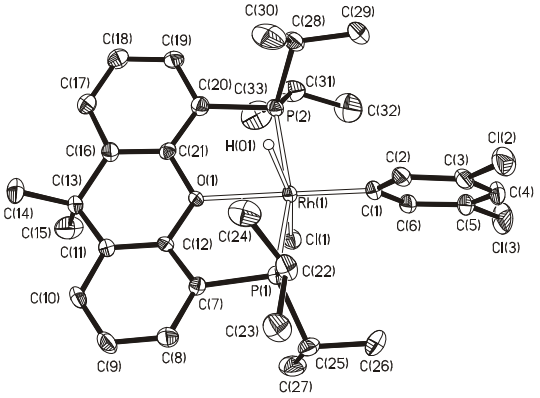


Figure 5. ORTEP diagram of complex **29** (50% probability ellipsoids). Hydrogen atoms (except the hydride) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)-P(1) = 2.2958(13), Rh(1)-P(2) = 2.2984(13), Rh(1)-Cl(1) = 2.5062(13), Rh(1)-O(1) = 2.239(3), Rh(1)-C(1) = 2.001(5); P(1)-Rh(1)-P(2) = 158.73(5), P(1)-Rh(1)-Cl(1) = 98.53(5), P(2)-Rh(1)-Cl(1) = 94.79(5), P(1)-Rh(1)-O(1) = 81.72(9), P(2)-Rh(1)-O(1) = 82.60(8), P(1)-Rh(1)-C(1) = 94.60(14), P(2)-Rh(1)-C(1) = 99.82(14), C(1)-Rh(1)-Cl(1) = 98.32(14), C(1)-Rh(1)-O(1) = 174.30(17), H(1)-Rh(1)-Cl(1) = 152.3(19).

The ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra of **27**-**29**, in benzene-d_6, at room temperature are consistent with the structures shown in Figures 4 and 5. According to the presence of the hydride ligand, the ^{1}H NMR spectra contain a double ($^{1}J_{H\text{-}Rh}$ = 21-26 Hz) triplet ($^{2}J_{H\text{-}P} \approx 12$ Hz) between -14 and -15.5 ppm. In the $^{13}C\{^{1}H\}$ NMR spectra, the resonance due to the metalated carbon atom of the phenyl groups is observed as a double ($^{1}J_{C\text{-}Rh}$ = 38-42 Hz) triplet ($^{3}J_{C\text{-}P}$ = 10-12 Hz) between 145 and 150 ppm. The $^{31}P\{^{1}H\}$ NMR spectra show a doublet ($^{1}J_{P\text{-}Rh} \approx 111$ Hz) between 42 and 48 ppm. In contrast to the 2,3-dichlorophenyl group of **27**, which lies with the chlorine atoms syn disposed with regard to the hydride ligand in the solid state and solution, the asymmetric 3,4-dichlorophenyl ligand of **28** rotates around the rhodium-aryl bond in solution, overcoming an activation energy close to 12 kcal·mol^{-1}.

Characteristic spectroscopic features of the square-planar rhodium(I) complexes **30** and **31** are double ($^{1}J_{C\text{-}Rh}$ = 46.6 (**30**) and 42.5 (**31**) Hz) doublets ($^{3}J_{C\text{-}P}$ = 14.9 (**30**) and 12.5 (**31**) Hz) at 165.1 ppm for **30** and 170.7 ppm for **31**, corresponding to the metalated carbon atom of the dichlorophenyl ligand, in the $^{13}C\{^{1}H\}$ NMR spectra and a doublet ($^{1}J_{P\text{-}Rh} \approx$ 171 Hz) at about 38 ppm in the $^{31}P\{^{1}H\}$ NMR spectra.

CONCLUDING REMARKS

This study has revealed that the square-planar POP-rhodium(I) monohydride RhH{xant(P^{i}Pr$_2$)$_2$} undergoes the C-Cl bond *cis*-oxidative addition of chlorobenzene, chlorotoluenes, chlorofluorobenzenes, and di- and trichlorobenzenes to give rhodium(III) RhHCl(aryl){xant(P^{i}Pr$_2$)$_2$} derivatives. The C-Cl bond activation is governed by steric reasons. As a consequence, initially, the less hindered C-Cl bond is selectively added in all cases.

The C-H bond activation of the chloroarenes is kinetically and thermodynamically disfavored with regard to the C-Cl bond addition. Thus, although the C-H bond activation reactions should give rise to the evolution of the volatile H_2 molecule with formation of square-planar rhodium(I)-aryl derivatives, these C-H bond activation products have been only observed for the reactions of RhH{xant(P^{i}Pr$_2$)$_2$} with 1,2-dichlorobenzene and chlorofluorobenzenes.[29] For the latter, the amount of the minor C-H bond activation product is sensitive to the position of the fluorine atom in the arene, increasing as is away from the chlorine atom.

The rhodium(III) products RhHCl(aryl){xant(P^{i}Pr$_2$)$_2$} show a marked ability to undergo reductive elimination of HCl, through an ionic mechanism involving the initial dissociation of the chloride ligand and the subsequent proton abstraction from the resulting cations [RhH(aryl){xant(P^{i}Pr$_2$)$_2$}]$^{+}$. As a consequence of this property, a wide range of square-planar rhodium(I)-aryl pure isomers have been prepared and characterized, in addition to their rhodium(III) precursors. These rhodium(III) cations along with rhodium(I)-η^2-arene species appear to be also the keys to reach the thermodynamic equilibria between the possible RhHCl(aryl){xant(P^{i}Pr$_2$)$_2$} isomers, after the C-Cl bond activation.

In conclusion, the square-planar POP-rhodium(I) monohydride RhH{xant(P^{i}Pr$_2$)$_2$} promotes the sterically governed C-Cl bond *cis*-oxidative addition of chloro- and di-and trichlorobenzenes to give rhodium(III) RhHCl(aryl){xant(P^{i}Pr$_2$)$_2$} derivatives, which undergo dehydrodechlorination to afford a wide range of square-planar rhodium(I) Rh(aryl){xant(P^{i}Pr$_2$)$_2$} isomers.

EXPERIMENTAL SECTION

General Information. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques or in a drybox. Pentane and toluene were obtained oxygen- and water-free from an MBraun solvent purification apparatus. Pentane was stored over P_2O_5 in the drybox. Acetone was dried, distilled, and stored under argon. Liquid chloroarenes were dried by standard procedures and distilled under argon prior to use. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR spectra were recorded on Bruker 300 ARX, Bruker Avance 300 MHz, Bruker Avance 400 MHz or Bruker Avance 500 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, $^{13}C\{^{1}H\}$), external 85% H_3PO_4 ($^{31}P\{^{1}H\}$), or $CFCl_3$ ($^{19}F\{^{1}H\}$). Coupling constants *J* and *N* are given in hertz. Attenuated total reflection infrared spectra (ATR-IR) of solid samples were run on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). RhH{xant(P^{i}Pr$_2$)$_2$} (**1**) was prepared by the published method.[20]

Reaction of RhH{xant(P^{i}Pr$_2$)$_2$} (1) with chlorobenzene: Preparation of RhHCl(C$_6$H$_5$){xant(P^{i}Pr$_2$)$_2$} (2). A solution of **1** (150 mg, 0.27 mmol) in pentane (4 mL) was treated with chlorobenzene (56 μL, 0.54 mmol) and the resulting mixture was stirred during 24 hours at room temperature. After this time, it was concentrated to dryness to afford a beige precipitate, that was further washed with pentane (6 x 1 mL) and finally it was dried in vacuo. Yield: 108 mg (60%). $^{31}P\{^{1}H\}$ MNR spectroscopy shows that the reaction is quantitative, but the isolated yield is moderate due to the solubility of the complex in pentane. Anal. Calcd. for $C_{33}H_{46}ClOP_2Rh$: C, 60.14; H, 7.03. Found: C, 59.71; H, 6.82. HRMS (electrospray, *m/z*) calcd. for $C_{33}H_{46}OP_2Rh$ [M-Cl]$^{+}$: 623.2073; found: 623.2086. IR (cm^{-1}): ν(Rh-H) 2092 (w), ν(C=C) 1566

(m), ν(C-O-C) 1192 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.34 (br, 2H, *o*-CH Ph), 7.09 (dd, J_{H-H} = 7.2, J_{H-H} = 7.2, 2H, *m*-CH Ph), 7.06 (m, 2H, CH-arom POP), 7.04 (d, J_{H-H} = 7.7, 2H, CH-arom POP), 6.99 (t, J_{H-H} = 7.2, 1H, *p*-CH Ph), 6.86 (t, J_{H-H} = 7.6, 2H, CH-arom POP), 2.76 (m, 2H, PC*H*$(CH_3)_2$), 2.26 (m, 2H, PC*H*$(CH_3)_2$), 1.56 (dvt, J_{H-H} = 7.4, *N* = 15.4, 6H, PCH(C*H*$_3)_2$), 1.29 (dvt, J_{H-H} = 7.8, *N* = 16.0, 6H, PCH(C*H*$_3)_2$), 1.28, 1.16 (both s, 3H each, CH_3), 1.06 (dvt, J_{H-H} = 6.5, *N* = 14.6, 6H, PCH(C*H*$_3)_2$), 0.99 (dvt, J_{H-H} = 6.2, *N* = 13.7, 6H, PCH(C*H*$_3)_2$), -15.66 (dt, $^1J_{H-Rh}$ = 25.5, $^2J_{H-P}$ = 12.8, 1H, Rh-H). ^{13}C{^{1}H} NMR (75.48 MHz, C_6D_6, 298 K): δ 155.3 (vt, *N* = 12.9, Carom POP), 145.1 (dt, $^1J_{C-Rh}$ = 35.4, $^2J_{C-P}$ = 9.9, Rh-C Ph), 142.6 (br s, CH Ph), 132.1 (vt, *N* = 5.4, Carom POP), 130.8 (s, CH-arom POP), 127.9 (s, CH-arom POP), 126.4 (s, CH Ph), 124.6 (vt, *N* = 5.0, CH-arom POP), 124.0 (vt, *N* = 25.5, Carom POP), 121.5 (s, CH Ph), 34.5 (s, *C*$(CH_3)_2$), 34.0 (s, C(*C*H$_3)_2$), 28.9 (vt, *N* = 21.5, P*C*H$(CH_3)_2$), 28.5 (s, C(*C*H$_3)_2$), 27.2 (dvt, J_{C-Rh} = 2.8, *N* = 26.2, P*C*H$(CH_3)_2$), 20.8 (s, PCH(*C*H$_3)_2$), 19.0 (vt, *N* = 4.8, PCH(*C*H$_3)_2$), 18.9 (s, PCH(*C*H$_3)_2$), 18.7 (vt, *N* = 4.6, PCH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (121.48 MHz, C_6D_6, 298 K): δ 40.6 (d, $^1J_{P-Rh}$ = 114.5)

Evolution of RhHCl(C_6H_5){xant(P^iPr_2)$_2$} (2) in acetone. A screwtop NMR tube charged with a solution of complex **2** (20 mg, 0.03 mmol) in acetone (0.4 mL) was placed into a thermostatic bath at 40 ºC, and it was periodically checked by ^{31}P{^{1}H} NMR spectroscopy. After 7 days, the ^{31}P{^{1}H} NMR spectrum shows the quantitative conversion to RhCl{xant(P^iPr_2)$_2$} (**3**) (doublet at δ 36.0, $^1J_{P-Rh}$ = 141.4 Hz).

Reaction of RhCl{xant(P^iPr_2)$_2$} (3) with benzene. A screwtop NMR tube charged with a solution of complex **3** (20 mg, 0.034 mmol) in benzene (0.4 mL) was periodically checked by ^{31}P{^{1}H} NMR spectroscopy. After 12 days, the ^{31}P{^{1}H} NMR spectrum shows a mixture of complexes **3** and **2** in a ratio 87:13.

Reaction of RhHCl(C_6H_5){xant(P^iPr_2)$_2$} (2) with KO^{t}Bu: Preparation of Rh(C_6H_5){xant(P^iPr_2)$_2$} (4). A solution of **2** (50 mg, 0.075 mmol) in acetone (5 mL) was treated with KO^{t}Bu (16 mg, 0.15 mmol) and the resulting mixture was stirred during 5 minutes at room temperature. After this time, it was concentrated to dryness to afford an orange residue. Toluene (5 mL) was added, and the resulting suspension was filtered to remove the potassium salts, getting a red solution, that was evaporated to dryness. Addition of pentane (3 mL) afforded an orange solid, that was washed with pentane (3 x 1 mL) and finally, it was dried in vacuo. Yield: 19 mg (40%). ^{31}P{^{1}H} MNR spectroscopy shows that the reaction is quantitative, but the isolated yield is low due to the solubility of the complex in pentane. ^{1}H and ^{31}P{^{1}H} NMR spectra agree well with those reported previously for this compound.[21]

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with 3-chlorotoluene: Preparation of RhHCl(C_6H_4-3-Me){xant(P^iPr_2)$_2$} (5). A solution of **1** (70 mg, 0.13 mmol) in pentane (5 mL) was treated with 3-chlorotoluene (150 µL, 1.3 mmol) and the resulting mixture was stirred during 3 hours at room temperature. After this time, it was concentrated to dryness to afford a beige residue. Addition of pentane afforded a beige solid that was washed with pentane (3 x 1 mL) and finally it was dried in vacuo. Yield: 52.6 mg (61%). Anal. Calcd. for $C_{34}H_{48}ClOP_2Rh$: C, 60.67; H, 7.19. Found: C, 60.78; H, 7.43. HRMS (electrospray, *m*/*z*) calcd. for $C_{34}H_{48}ClOP_2Rh$ [M-Cl]$^+$: 637.2230. Found 637.2251. IR (cm^{-1}): ν(Rh-H) 2114 (w), ν(C=C) 1572 (m), ν(C-O-C) 1196 (m). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 8.49 (br, 2H, *o*-CH Ph), 7.20 (m, 2H, CH-arom POP), 7.17 (d, J_{H-H} = 7.6, 2H, CH-arom POP), 7.11 (t, J_{H-H} = 7.3, 1H, *m*-CH Ph), 6.99 (t, J_{H-H} = 7.6, 2H, CH-arom POP), 6.91 (d, J_{H-H} = 7.3, 1H, *p*-CH Ph), 2.89 (m, 2H, PC*H*$(CH_3)_2$), 2.48 (s, 3H, C_6H_4-3-C*H*$_3$), 2.39 (m, 2H, PC*H*$(CH_3)_2$), 1.69 (dvt, J_{H-H} = 6.7, *N* = 14.6, 6H, PCH(C*H*$_3)_2$), 1.41 (dvt, J_{H-H} = 7.7, *N* = 15.9, 6H, PCH(C*H*$_3)_2$), 1.40, 1.27 (both s, 3H each, CH_3), 1.18 (dvt, J_{H-H} = 7.4, *N* = 15.4, 6H, PCH(C*H*$_3)_2$), 1.11 (dvt, J_{H-H} = 7.1, *N* = 14.5, 6H, PCH(C*H*$_3)_2$), -15.59 (dt, $^1J_{H-Rh}$ = 26.3, $^2J_{H-P}$ = 13.1, 1H, Rh-H). ^{13}C{^{1}H} NMR (75.48 MHz, C_6D_6, 298 K): δ 155.1 (vt, *N* = 12.8, Carom POP), 144.5 (dt, $^1J_{C-Rh}$ = 35.5, $^2J_{C-P}$ = 10.0, Rh-C Ph), 134.7 (s, *C*-CH$_3$ Ph), 132.1 (vt, *N* = 5.5, Carom POP), 130.8 (s, CH-arom POP), 128.4 (s, CH Ph), 127.9 (s, CH-arom POP), 126.1 (s, CH Ph), 124.6 (vt, *N* = 4.6, CH-arom POP), 124.2 (vt, *N* = 25.5, Carom POP), 122.4 (s, CH Ph), 34.5 (s, *C*arom POP), 34.3 (s, *C*$(CH_3)_2$), 28.9 (vt, *N* = 21.6, P*C*H$(CH_3)_2$), 28.5 (s, C(*C*H$_3)_2$), 27.2 (dvt, J_{C-Rh} = 2.7, *N* = 26.9, P*C*H$(CH_3)_2$), 22.0 (s, CH_3 Ph), 20.8, 19.1, 18.8 (all s, PCH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (161.41 MHz, C_6D_6, 298 K): δ 40.8 (d, $^1J_{P-Rh}$ = 117.8).

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with 4-chlorotoluene: Preparation of RhHCl(C_6H_4-4-Me){xant(P^iPr_2)$_2$} (6). A solution of **1** (130 mg, 0.24 mmol) in pentane (5 mL) was treated with 4-chlorotoluene (56 µL, 0.47 mmol) and the resulting mixture was stirred during 28 hours at room temperature. After this time, it was concentrated to dryness to afford a beige residue. Addition of pentane afforded a beige solid that was washed with pentane (3 x 1 mL) and finally it was dried in vacuo. Yield: 72.3 mg (47%). ^{31}P{^{1}H} MNR spectroscopy shows that the reaction is quantitative, but the isolated yield is moderate due to the solubility of the complex in pentane. Anal. Calcd. for $C_{34}H_{48}ClOP_2Rh$: C, 60.67; H, 7.19. Found: C, 60.39; H, 6.89. HRMS (electrospray, *m*/*z*) calcd. for $C_{34}H_{48}OP_2Rh$ [M-Cl]$^+$: 637.2230; found 637.2222. IR (cm^{-1}): ν(Rh-H) 2100 (w), ν(C=C) 1582 (m), ν(C-O-C) 1192 (m). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 8.48 (br, 2H, *o*-CH Ph), 7.20 (m, 2H, CH-arom POP), 7.17 (d, J_{H-H} = 7.8, 2H, CH-arom POP), 7.04 (d, J_{H-H} = 7.9, 2H, *m*-CH Ph), 6.99 (t, J_{H-H} = 7.6, 2H, CH-arom POP), 2.88 (m, 2H, PC*H*$(CH_3)_2$), 2.39 (m, 2H, PC*H*$(CH_3)_2$), 2.36 (s, 3H, C_6H_4-4-C*H*$_3$), 1.69 (dvt, J_{H-H} = 7.4, *N* = 15.3, 6H, PCH(C*H*$_3)_2$), 1.41 (s, 3H, CH_3), 1.40 (dvt, J_{H-H} = 7.7, *N* = 15.5, 6H, PCH(C*H*$_3)_2$), 1.27 (s, 3H, CH_3), 1.19 (dvt, J_{H-H} = 7.3, *N* = 15.5, 6H, PCH(C*H*$_3)_2$), 1.11 (dvt, J_{H-H} = 7.1, *N* = 14.6, 6H, PCH(C*H*$_3)_2$), -15.59 (dt, $^1J_{H-Rh}$ = 26.4, $^2J_{H-P}$ = 13.2, 1H, Rh-H). ^{13}C{^{1}H} NMR (75.48 MHz, C_6D_6, 298 K): δ 155.1 (vt, *N* =12.6, *C*arom POP), 139.9 (dt, $^1J_{C-Rh}$ = 35.0, $^2J_{C-P}$ = 10.1, Rh-C Ph), 132.2 (vt, *N* = 5.2, *C*arom POP), 130.8 (s, *C*H-arom POP), 129.9 (s, *C*-CH$_3$ Ph), 128.4 (s, *C*H Ph), 127.8 (s, *C*H Ph), 127.4 (s, *C*H-arom POP), 124.6 (s, *C*H-arom POP), 124.2 (vt, *N* = 25.4, *C*arom POP), 34.5 (s, *C*arom POP), 34.1 (s, *C*$(CH_3)_2$), 29.0 (vt, J_{C-Rh} = 22.1, P*C*H$(CH_3)_2$), 28.4 (s, C(*C*H$_3)_2$), 27.3 (dvt, J_{C-Rh} = 2.5, *N* = 25.9, P*C*H$(CH_3)_2$), 21.0 (s, *C*H$_3$-Ph), 20.9, 19.1, 19.0, 18.9 (all s, PCH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (161.41 MHz, C_6D_6, 298 K): δ 40.8 (d, $^1J_{P-Rh}$ = 116.5).

Reaction of RhHCl(C_6H_4-3-Me){xant(P^iPr_2)$_2$} (5) with KO^{t}Bu: Preparation of Rh(C_6H_4-3-Me){xant(P^iPr_2)$_2$} (7). This compound was prepared analogously as described for **4**, starting from **5** (100 mg, 0.15 mmol) and KO^{t}Bu (31.8 mg, 0.30 mmol). Orange solid. Yield: 87.2 mg (91%). ^{1}H and ^{31}P{^{1}H} NMR spectra are well with those reported previously for this compound.[21]

Reaction of RhHCl(C_6H_4-4-Me){xant(P^iPr_2)$_2$} (6) with KO^{t}Bu: Preparation of Rh(C_6H_4-4-Me){xant(P^iPr_2)$_2$} (8). This compound was prepared analogously as described for **4**, starting from **6** (100 mg, 0.148 mmol) and KO^{t}Bu (31.8 mg, 0.30 mmol). Orange solid. Yield: 84.2 mg (89%). ^{1}H and ^{31}P{^{1}H} NMR spectra agree well with those reported previously for this compound.[21]

Evolution of RhHCl(C_6H_4-3-Me){xant(P^iPr_2)$_2$} (5) in acetone. A screwtop NMR tube charged with a solution of complex **5** (20 mg, 0.03 mmol) in acetone (0.4 mL) and it was periodically checked by ^{31}P{^{1}H} NMR spectroscopy. After 1 day at room temperature, the ^{31}P{^{1}H} NMR spectrum shows a mixture of RhHCl(C_6H_4-3-Me){xant(P^iPr_2)$_2$} (**5**), RhHCl(C_6H_4-4-Me){xant(P^iPr_2)$_2$} (**6**), Rh(C_6H_4-3-Me){xant(P^iPr_2)$_2$} (**7**) and Rh(C_6H_4-4-Me){xant(P^iPr_2)$_2$} (**8**) in a ratio 43:20:15:22.

Evolution of RhHCl(C_6H_4-4-Me){xant(P^iPr_2)$_2$} (6) in acetone. A screwtop NMR tube charged with a solution of complex **6** (20 mg, 0.03 mmol) in acetone (0.4 mL) and it was periodically checked by ^{31}P{^{1}H} NMR spectroscopy. After 1 day at room temperature, the ^{31}P{^{1}H} NMR spectrum shows a mixture of RhHCl(C_6H_4-3-Me){xant(P^iPr_2)$_2$} (**5**), RhHCl(C_6H_4-4-Me){xant(P^iPr_2)$_2$} (**6**), Rh(C_6H_4-3-Me){xant(P^iPr_2)$_2$} (**7**) and Rh(C_6H_4-4-Me){xant(P^iPr_2)$_2$} (**8**) in a ratio 43:20:15:22.

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with 1,2-fluorochlorobenzene: Preparation of RhHCl(C_6H_4-2-F){xant(P^iPr_2)$_2$} (9). A solution of **1** (130 mg, 0.24 mmol) in pentane (5 mL) was treated with 1,2-fluorochlorobenzene (62.1 mg, 0.48 mmol) and the resulting mixture was stirred during 8 h at room temperature. This mixture was concentrated to dryness to afford a beige solid. Addition of pentane afforded a beige solid, that was washed with pentane (3 x 1 mL) and finally it was dried in vacuo. Yield: 59 mg (36%). ^{31}P{^{1}H} MNR spectroscopy shows that the reaction is quantitative, but the isolated yield is low due to the high solubility of the complex in pentane. Anal. Calcd. for $C_{33}H_{45}ClFOP_2Rh$: C, 58.54; H, 6.70. Found: C, 58.45; H, 6.36 HRMS (electrospray, *m/z*) calcd. for $C_{33}H_{45}FOP_2Rh$ [M-Cl]$^+$: 641.1979; found: 641.1989. IR (cm^{-1}): ν(Rh-H) 2160 (w), ν(C=C) 1577 (m), ν(C-O-C) 1431 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 9.34 (dd, J_{H-F} = 6.2, J_{H-H} = 6.2, 1H, *o*-CH Ph), 7.10-6.88 (m, 9H, 6 CH-arom POP + 3H CH Ph), 2.74 (m, 2H, PC*H*(CH$_3$)$_2$), 2.29 (m, 2H, PC*H*(CH$_3$)$_2$), 1.56 (dvt, J_{H-H} = 7.4, *N* = 15.3, 6H, PCH(C*H*$_3$)$_2$), 1.30, 1.21 (both s, 3H each, CH$_3$), 1.20 (dvt, J_{H-H} = 7.7, *N* = 15.5, 6H, PCH(C*H*$_3$)$_2$), 1.08 (dvt, J_{H-H} = 8.9, *N* = 17.0, 6H, PCH(C*H*$_3$)$_2$), 1.03 (dvt, J_{H-H} = 8.6, *N* = 16.0, 6H, PCH(C*H*$_3$)$_2$), -14.78 (ddt, $^1J_{H-Rh}$ = 21.8, $^2J_{H-P}$ = 12.8, $^4J_{H-F}$ = 6.2, 1H, Rh-H). ^{13}C{^{1}H} NMR (100.62 MHz, toluene-d_8, 298 K): δ 166.6 (d, J_{C-F} = 229.3, *C*-F Ph), 155.5 (vt, *N* = 12.6, Carom POP), 143.9 (d, J_{C-F} = 12.0, CH Ph), 132.2 (s, Carom POP), 131.6 (s, CH-arom POP), 128.6 (s, CH-arom POP), 124.9 (s, CH-arom POP), 124.3 (t, *N* = 25.6, Carom POP), 123.9 (d, J_{C-F} = 7.5, CH Ph), 122.7 (s, CH Ph), 113.4 (d, J_{C-F} = 31.0, CH Ph), 34.9 (s, *C*(CH$_3$)$_2$), 34.4 (s, C(*C*H$_3$)$_2$), 29.8 (s, C(*C*H$_3$)$_2$), 29.3 (vt, *N* = 21.9, P*C*H(CH$_3$)$_2$), 28.4 (dvt, J_{C-Rh} = 2.7, *N* = 26.3, P*C*H(CH$_3$)$_2$), 21.3, 19.2, 18.9, 18.8 (all s, PCH(*C*H$_3$)$_2$), the signal for the Rh-C atom was not observed. ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6, 298 K): δ 43.8 (d, $^1J_{P-Rh}$ = 111.0). ^{19}F{^{1}H} NMR (282.2 MHz, C_6D_6, 298 K): δ -85.2 (d, J_{F-Rh} = 19.1).

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with 1,3-fluorochlorobenzene. A solution of **1** (130 mg, 0.24 mmol) in pentane (5 mL) was treated with 1,3-fluorochlorobenzene (62.1 mg, 0.48 mmol) and the resulting mixture was stirred during 3 h at room temperature. After this time, the reaction was checked by ^{31}P{^{1}H} NMR spectroscopy, showing a mixture of RhHCl(C_6H_4-3-F){xant(P^iPr_2)$_2$} (**10**) and Rh(C_6H_3-2-Cl-6-F){xant(P^iPr_2)$_2$} (**12**) in a ratio 91:9. This mixture was concentrated to dryness to afford a beige solid. Addition of pentane afforded a beige solid that was washed with pentane (3 x 1 mL) and finally it was dried in vacuo. Yield: 132.2 mg (82%). A ^{31}P{^{1}H} NMR spectrum of a solution of this solid in C_6D_6 shows only complex RhHCl(C_6H_4-3-F){xant(P^iPr_2)$_2$} (**10**). Data for RhHCl(C_6H_4-3-F){xant(P^iPr_2)$_2$} (**10**): Anal. Calcd. for $C_{33}H_{45}ClFOP_2Rh$: C, 58.54; H, 6.70. Found: C, 58.11; H, 6.36. HRMS (electrospray, *m/z*) calcd. for $C_{33}H_{45}FOP_2Rh$ [M-Cl]$^+$: 641.1979; found: 641.1958. IR (cm^{-1}): ν(Rh-H) 2138 (w), ν(C=C) 1582 (m), ν(C-O-C) 1191 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.15 (br, 2H, *o*-CH Ph), 7.16 (m, 2H, CH-arom POP), 7.15 (d, J_{H-H} = 7.2, 2H, CH-arom POP), 6.88 (dd, J_{H-F} = 15.0, J_{H-H} = 7.8, 1H, *p*-CH Ph), 6.86 (t, J_{H-H} = 7.6, 2H, CH-arom POP), 6.71 (dt, J_{H-H} = 7.8, J_{H-F} = 2.2, 1H, *m*-CH Ph), 2.73 (m, 2H, PC*H*(CH$_3$)$_2$), 2.21 (m, 2H, PC*H*(CH$_3$)$_2$), 1.53 (dvt, J_{H-H} = 7.3, *N* = 15.5, 6H, PCH(C*H*$_3$)$_2$), 1.28 (s, 3H, CH$_3$), 1.34 (dvt, J_{H-H} = 7.5, *N* = 16.4, 6H, PCH(C*H*$_3$)$_2$), 1.15 (s, 3H, CH$_3$), 1.02 (dvt, J_{H-H} = 7.5, *N* = 16.0, 6H, PCH(C*H*$_3$)$_2$), 0.95 (dvt, J_{H-H} = 7.3, *N* = 14.8, 6H, PCH(C*H*$_3$)$_2$), -15.58 (dt, $^1J_{H-Rh}$ = 26.0, $^2J_{H-P}$ = 12.9, 1H, Rh-H). ^{13}C{^{1}H} NMR (75.4 MHz, toluene-d_8, 298 K): δ 161.3 (d, J_{C-F} = 246.0, *C*-F Ph), 155.7 (vt, *N* =12.8, Carom POP), 147.8 (dtd, $^1J_{C-Rh}$ = 36.5, $^2J_{C-P}$ = 9.6, $^3J_{C-F}$ = 4.2, Rh-*C* Ph), 132.5 (vt, *N* = 5.0, Carom POP), 131.1 (s, CH-arom POP), 128.3 (s, CH-arom POP), 126.6 (d, J_{C-F} = 7.2, *m*-CH Ph), 125.0 (s, CH-arom POP), 124.2 (t, *N* = 12.8, Carom POP), 108.3 (d, J_{C-F} = 20.9, *m*-*C*H Ph)), 35.0 (s, *C*(CH$_3$)$_2$), 34.3 (s, C(*C*H$_3$)$_2$), 29.4 (vt, *N* = 21.9, P*C*H(CH$_3$)$_2$), 28.7 (s, C(*C*H$_3$)$_2$), 27.8 (dvt, J_{C-Rh} = 2.8, *N* = 26.1, P*C*H(CH$_3$)$_2$), 21.1, 19.8, 19.0 (all s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 298 K): δ 41.4 (d, $^1J_{P-Rh}$ = 113.7). ^{19}F{^{1}H} NMR (282.2 MHz, C_6D_6, 298 K): δ -121.0 (s).

Characteristic NMR data for Rh(C_6H_3-2-Cl-6-F){xant(P^iPr_2)$_2$} (**12**): ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.42 (ddd, J_{H-F} = 11.3, J_{H-H} = 7.8, J_{H-H} = 1.8, 1H, *m*-CH Ph), 7.0 (dd, J_{H-H} = 7.4, J_{H-H} = 7.4, 1H, *p*-CH Ph). ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 298 K): δ 40.9 (dd, $^1J_{P-Rh}$ = 164.5, $^4J_{P-F}$ = 3.0).

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with 1,4-fluorochlorobenzene. A solution of **1** (100 mg, 0.18 mmol) in pentane (5 mL) was treated with 1,4-fluorochlorobenzene (39.2 mg, 0.36 mmol) and the resulting mixture was stirred for 8 hours at room temperature. After this time, the reaction was checked by ^{31}P{^{1}H} NMR spectroscopy, showing a mixture of RhHCl(C_6H_4-4-F){xant(P^iPr_2)$_2$} (**13**) and Rh(C_6H_4-3-Cl-6-F){xant(P^iPr_2)$_2$} (**15**) in a ratio 61:39. This mixture was concentrated to dryness to afford a beige solid. The addition of pentane (5 x 1 mL) allowed the isolation of complex **13** in pure form, due to the higher solubility of **15** in this solvent. Data for RhHCl(C_6H_4-4-F){xant(P^iPr_2)$_2$} (**13**): Yield: 69 mg (56%). Anal. Calcd. for $C_{33}H_{45}ClFOP_2Rh$: C, 58.54; H, 6.70. Found: C, 58.45; H, 6.26. HRMS (electrospray, *m/z*) calcd. for $C_{33}H_{45}ClFOP_2Rh$ [M-Cl]$^+$: 641.1979; found 641.1983. IR (cm^{-1}): ν(Rh-H) 2093 (w), ν(C=C) 1573 (m), ν(C-O-C) 1188 (m). ^{1}H NMR (300.13 MHz, toluene-d_8, 298 K): δ 8.01 (br, 2H, *o*-CH Ph), 7.09(d, J_{H-H} = 7.5, 2H, CH-arom POP), 7.08 (m, 2H, CH-arom POP), 6.91 (t, J_{H-H} = 7.5, 2H, CH-arom POP), 6.76 (t, J_{H-H} = 8.7, 2H, *m*-CH Ph POP), 2.65 (m, 2H,

PC*H*(CH_3)$_2$), 2.19 (m, 2H, PC*H*(CH_3)$_2$), 1.48 (dvt, J_{H-H} = 7.4, N = 15.3, 6H, PCH(C*H*$_3$)$_2$), 1.31 (s, 3H, CH_3), 1.21 (dvt, J_{H-H} = 7.4, N = 15.9, 6H, PCH(C*H*$_3$)$_2$), 1.14 (s, 3H, CH_3), 0.99 (dvt, J_{H-H} = 7.7, N = 16.3, 6H, PCH(C*H*$_3$)$_2$), 0.96 (dvt, J_{H-H} = 8.0, N = 16.0, 6H, PCH(C*H*$_3$)$_2$), -15.70 (dt, $^1J_{H-Rh}$ = 26.3, $^2J_{H-P}$ = 13.2, 1H, Rh-H). $^{13}C\{^1H\}$ NMR (100.62 MHz, toluene-d_8, 298 K): δ 167.7 (d, J_{C-F} = 221.3, *C*-F Ph), 156.8 (vt, N =15.8, Carom POP), 156.2 (m, Rh-*C* Ph), 132.5 (vt, N = 5.0, Carom POP), 131.6 (s, CH-arom POP), 128.2 (s, CH-arom POP), 124.4 (s, CH-arom POP), 124.2 (t, N = 12.8, Carom POP), 105.0 (d, J_{C-F} = 21.1, *m*-CH Ph), 35.0 (s, *C*(CH_3)$_2$), 34.3 (s, C(*C*H$_3$)$_2$), 29.4 (vt, J_{C-Rh} = 21.7, P*C*H(CH_3)$_2$), 28.6 (s, C(*C*H$_3$)$_2$), 27.8 (dvt, J_{C-Rh} = 6.3, N = 26.6, P*C*H(CH_3)$_2$), 21.2, 19.6, 19.0, 18.9 (all s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 40.8 (d, $^1J_{P-Rh}$ = 114.0). $^{19}F\{^1H\}$ NMR (282.2 MHz, C_6D_6, 298 K): δ -125.1 (s)

Characteristic NMR data for Rh(C_6H_4-3-Cl-6-F){xant(P^{i}Pr$_2$)$_2$} (**15**): ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.78 (dt, J_{H-Rh} = 2.9, J_{H-P} = 2.9, *o*-CH Ph), 6.30 (dd, J_{H-H} = 8.3, J_{H-F} = 1.3, 1H, *p*-CH Ph), 6.08 (dd, J_{H-H} = 8.3, J_{H-F} = 9.0, 1H, *m*-CH Ph). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 40.7 (dd, $^1J_{P-Rh}$ = 164.8, $^4J_{P-F}$ = 4.0).

Reaction of RhHCl(C_6H_4-2-F){xant(P^{i}Pr$_2$)$_2$} (9). with KO^{t}Bu: Preparation of Rh(C_6H_4-2-F){xant(P^{i}Pr$_2$)$_2$} (16). This compound was prepared analogously as described for **4**, starting from **9** (50 mg, 0.074 mmol) and KO^{t}Bu (16 mg, 0.15 mmol). Orange solid. Yield: 53.3 mg (89%). ^{1}H and $^{31}P\{^1H\}$ NMR spectra are well with those reported previously for this compound.[21]

Reaction of RhHCl(C_6H_4-3-F){xant(P^{i}Pr$_2$)$_2$} (10) with KO^{t}Bu: Preparation of Rh(C_6H_4-3-F){xant(P^{i}Pr$_2$)$_2$} (17). This compound was prepared analogously as described for **4**, starting from **10** (100 mg, 0.15 mmol) and KO^{t}Bu (31 mg, 0.28 mmol), but stirring 1 h at room temperature. Orange solid. Yield: 83.2 mg (88%). Anal. Calcd. for $C_{33}H_{44}FOP_2Rh$: C, 61.88; H, 6.92. Found: C, 61.45; H, 7.06. HRMS (electrospray, *m*/*z*): calcd. for $C_{33}H_{44}FOP_2Rh$ [M-Cl]$^+$: 640.1901; found: 640.1872. IR (cm^{-1}): ν(C=C) 1573 (m), ν(C-O-C) 1192 (m). ^{1}H NMR (300.13 MHz; C_6D_6, 298 K): δ 7.90 (dt, J_{H-F} = 10.8, J_{H-P} = 2.6, 1H, *o*-CH Ph), 7.82 (d, J_{H-H} = 7.5, 1H, *o*-CH Ph), 7.23 (m, 2H, CH-arom POP), 7.04 (t, J_{H-H} = 7.5, 1H, *m*-CH Ph), 7.02 (dd, J_{H-H} = 7.7, J_{H-H} = 1.3, 2H, CH-arom POP), 6.83 (t, J_{H-H} = 7.6, 2H, CH-arom POP), 6.69 (dd, J_{H-H} = 7.8, J_{H-F} = 7.8, 1H, *p*-CH Ph), 2.35 (m, 4H, PC*H*(CH_3)$_2$), 1.21 (s, 6H, CH_3), 1.19 (dvt, J_{H-H} = 8.8, N = 15.9, 12H, PCH(C*H*$_3$)$_2$), 1.14 (dvt, J_{H-H} = 7.0, N = 14.1, 12H, PCH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6, 298 K): δ 167.0 (dtd, $^1J_{C-Rh}$ = 41.4, $^2J_{C-P}$ = 12.7, $^3J_{C-F}$ = 3.3, Rh-*C* Ph), 161.9 (dt, J_{C-F} = 245.7, J_{C-P} = 3.9, *C*-F Ph), 156.2 (vt, N =15.7, *C*arom POP), 135.4 (dt, J_{C-Rh} = 2.1, J_{C-P} = 2.1*o*-*C*H Ph), 131.3 (s, CH-arom POP), 130.7 (vt, N = 5.4, Carom POP), 127.9 (s, CH-arom POP), 125.6 (d, J_{C-F} = 7.7, *m*-CH Ph), 125.4 (vt, N = 15.6, Carom POP) , 125.1 (dt, J_{C-F} = 13.4, J_{C-P} = 3.0, *o*-CH Ph), 124.1 (vt, N = 3.6, CH-arom POP), 104.5 (d, J_{C-F} = 21.1, *p*-CH Ph), 34.0 (s, *C*(CH_3)$_2$), 33.0 (s, C(*C*H$_3$)$_2$), 25.2 (dvt, J_{C-Rh} = 2.8, N = 18.0, P*C*H(CH_3)$_2$), 19.3 (vt, N = 8.3, P*C*H(CH_3)$_2$), 18.5 (s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 37.3 (d, $^1J_{P-Rh}$ = 174.1). $^{19}F\{^1H\}$ NMR (282.2 MHz, C_6D_6, 298 K): δ -118.4 (s).

Reaction of RhHCl(C_6H_4-4-F){xant(P^{i}Pr$_2$)$_2$} (13) with K^{t}BuO: Preparation of Rh(C_6H_4-4-F){xant(P^{i}Pr$_2$)$_2$} (18). This compound was prepared analogously as described for **4**, starting from **13** (100 mg, 0.15 mmol) and K^{t}BuO (31 mg, 0.28 mmol). Orange solid. Yield: 88 mg (93%). Anal. Calcd. for $C_{33}H_{44}FOP_2Rh$: C, 61.88; H, 6.92. Found: C, 62.23; H, 7.10. HRMS (electrospray, *m*/*z*) calcd. for $C_{33}H_{44}FOP_2Rh$ [M]$^+$: 640.1901; found: 640.1892. IR (cm^{-1}): ν(C=C) 1579 (m), ν(C-O-C) 1191 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.93 (ddt, J_{H-H} = 7.3, J_{H-F} = 7.3, J_{H-Rh} = 2.9, 2H, *o*-CH Ph), 7.35 (m, 2H, CH-arom POP), 7.24 (t, J_{H-H} = 7.3, 2H, *m*-CH Ph), 7.09 (dd, J_{H-H} = 7.3, J_{H-H} = 1.2, 2H, CH-arom POP), 6.95 (t, J_{H-H} = 7.5, 2H, CH-arom), 2.45 (m, 4H, PC*H*(CH_3)$_2$), 1.33 (s, 6H, CH_3), 1.28 (dvt, J_{H-H} = 7.6, N = 14.7, 12H, PCH(C*H*$_3$)$_2$), 1.26 (dvt, J_{H-H} = 7.0, N = 13.9, 12H, PCH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6, 298 K): δ 159.3 (d, J_{C-F} = 233.7, *C*-F Ph), 156.3 (vt, N = 16.6, Carom POP), 153.3 (dt, $^1J_{C-Rh}$ = 42.0, $^2J_{C-P}$ = 10.7, Rh-*C* Ph), 139.2 (d, J_{C-F} = 2.3, *o*-CH Ph), 131.3 (s, CH-arom POP), 130.8 (s, Carom POP), 127.9 (s, CH-arom POP), 125.8 (t, N = 8.3, Carom POP), 124.1 (s, CH-arom POP), 112.5 (d, J_{C-F} = 16.8, *m*-CH Ph), 34.1 (s, *C*(CH_3)$_2$), 33.0 (s, C(*C*H$_3$)$_2$), 25.3 (dvt, J_{C-Rh} = 4.0, N = 19.3, P*C*H(CH_3)$_2$), 19.4, 18.6 (both s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 36.6 (d, $^1J_{P-Rh}$ = 174.3). $^{19}F\{^1H\}$ NMR (282.2 MHz, C_6D_6, 298 K): δ -128.8 (s).

Evolution of RhHCl(C_6H_4-2-F){xant(P^{i}Pr$_2$)$_2$} (9) in acetone. A screwtop NMR tube charged with a solution of complex **9** (20 mg, 0.029 mmol) in acetone (0.4 mL) and it was periodically checked by $^{31}P\{^1H\}$ NMR spectroscopy. After 7 days at room temperature, the $^{31}P\{^1H\}$ NMR spectrum shows a mixture of RhHCl(C_6H_4-2-F){xant(P^{i}Pr$_2$)$_2$} (**9**), RhHCl(C_6H_4-3-F){xant(P^{i}Pr$_2$)$_2$} (**10**) and Rh(C_6H_4-2-F){xant(P^{i}Pr$_2$)$_2$} (**16**) in a ratio 57:16:27.

Evolution of RhHCl(C_6H_4-3-F){xant(P^{i}Pr$_2$)$_2$} (10) in acetone. A screwtop NMR tube charged with a solution of complex **10** (20 mg, 0.029 mmol) in acetone (0.4 mL) and it was periodically checked by $^{31}P\{^1H\}$ NMR spectroscopy. After 7 days at room temperature, the $^{31}P\{^1H\}$ NMR spectrum shows a mixture of RhHCl(C_6H_4-3-F){xant(P^{i}Pr$_2$)$_2$} (**10**), RhHCl(C_6H_4-2-F){xant(P^{i}Pr$_2$)$_2$} (**9**), Rh(C_6H_4-2-F){xant(P^{i}Pr$_2$)$_2$} (**16**), Rh(C_6H_4-3-F){xant(P^{i}Pr$_2$)$_2$} (**17**) and Rh(C_6H_3-2-Cl-6-F){xant(P^{i}Pr$_2$)$_2$} (**12**) in a ratio 34:8:27:17:14.

Evolution of RhHCl(C_6H_4-4-F){xant(P^{i}Pr$_2$)$_2$} (13) in acetone. A screwtop NMR tube charged with a solution of complex **13** (20 mg, 0.029 mmol) in acetone (0.4 mL) and it was periodically checked by $^{31}P\{^1H\}$ NMR spectroscopy. After 7 days at room temperature, the $^{31}P\{^1H\}$ NMR spectrum shows a mixture of RhHCl(C_6H_4-4-F){xant(P^{i}Pr$_2$)$_2$} (**13**), RhHCl(C_6H_4-3-F){xant(P^{i}Pr$_2$)$_2$} (**10**), Rh(C_6H_4-2-F){xant(P^{i}Pr$_2$)$_2$} (**16**), Rh(C_6H_4-3-F){xant(P^{i}Pr$_2$)$_2$} (**17**) and Rh(C_6H_3-3-Cl-6-F){xant(P^{i}Pr$_2$)$_2$} (**15**) in a ratio 7:7:21:22:43.

Reaction of RhH{xant(P^{i}Pr$_2$)$_2$} (1) with 1,2-dichlorobenzene. A solution of **1** (100 mg, 0.18 mmol) in pentane (4 mL) was treated with 1,2-dichlorobenzene (23 μL, 0.18 mmol) and the resulting mixture was stirred during 3 days at room temperature. After this time, the reaction was checked by $^{31}P\{^1H\}$ NMR spectroscopy, showing a mixture of RhHCl(C_6H_4-2-Cl){xant(P^{i}Pr$_2$)$_2$} (**19**), Rh(C_6H_4-2-Cl){xant(P^{i}Pr$_2$)$_2$} (**20**), and Rh(C_6H_3-2,3-Cl$_2$){xant(P^{i}Pr$_2$)$_2$} (**22**) in a ratio 32:51:17. This mixture was evaporated to dryness and was dissolved in acetone (5 mL). To this solution K^{t}BuO (20 mg, 0.18 mmol) was added, and it was stirred during 5 min at room temperature. After this time, it was concentrated to dryness to afford an orange residue. Toluene (2 mL) was added, and the resulting suspension was filtered to remove the potassium salts, getting an orange solution,

that was evaporated to dryness. Addition of pentane (3 mL) afforded an orange solid, that was washed with pentane (3 x 1 mL) and finally, it was dried in vacuo. Yield: 97 mg. $^{31}P\{^1H\}$ NMR spectrum of this solid shows a mixture of the square planar derivatives Rh(C_6H_4-2-Cl){xant(P^iPr_2)$_2$} and Rh(C_6H_3-2,3-Cl_2){xant(P^iPr_2)$_2$} in a ratio 75:25.

*Spectroscopic data for Rh(C_6H_4-2-Cl){xant(P^iPr_2)$_2$} (**20**).* HRMS (electrospray, *m/z*) calcd. for $C_{33}H_{44}ClOP_2Rh$ $[M]^+$: 656.1605; found 656.1610. IR (cm^{-1}): ν(C=C) 1553 (m), ν(C-O-C) 1192 (m). ^1H NMR (400.13 MHz, C_6D_6, 298 K): δ 7.99 (dt, J_{H-H} = 7.3, J_{H-P} = 2.2, H, CH Ph), 7.42 (d, J_{H-H} = 7.7, 1H, CH Ph), 7.24 (m, 2H, CH-arom POP), 7.04 (dd, J_{H-H} = 7.6, J_{H-H} = 1.4, 2H, CH-arom POP), 6.99 (td, J_{H-H} = 7.7, J_{H-H} = 1.3, 1H, CH Ph), 6.85 (t, J_{H-H} = 7.6, 2H, CH-arom POP), 6.81 (t, J_{H-H} = 7.7, 1H, CH Ph), 2.51, 2.41 (both m, 2H, PC*H*(CH_3)$_2$), 1.30 (s, 3H, CH_3), 1.24 (dvt, J_{H-H} = 7.7, *N* = 16.4, 6H, PCH(C*H*$_3$)$_2$), 1.23 (dvt, J_{H-H} = 6.8, *N* = 14.5, 6H, PCH(C*H*$_3$)$_2$), 1.19 (s, 3H, CH_3), 1.16 (dvt, J_{H-H} = 8.4, *N* = 17.1, 6H, PCH(C*H*$_3$)$_2$), 1.10 (dvt, J_{H-H} = 6.9, *N* = 16.1, 6H, PCH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 298 K): δ 161.6 (dt, $^1J_{C-Rh}$ = 43.8, $^2J_{C-P}$ = 13.0, Rh-C Ph), 156.5 (vt, *N* = 15.8, Carom POP), 144.2 (s, *C*Cl Ph), 142.0 (s, CH Ph), 131.1 (s, CH-arom POP), 130.8 (s, Carom POP), 127.7 (s, CH-arom POP), 126.4 (s, CH Ph), 125.4 (vt, *N* = 14.9, Carom POP), 124.2 (s, CH Ph), 123.1 (s, CH-arom POP), 120.2 (s, CH Ph), 35.0 (s, C(*C*H$_3$)$_2$), 34.1 (s, *C*(CH$_3$)$_2$), 30.2 (s, PCH(*C*H$_3$)$_2$), 26.5 (vt, *N* = 17.8, P*C*H(CH$_3$)$_2$), 24.4 (vt, *N* = 14.1, P*C*H(CH$_3$)$_2$), 19.1 (vt, *N* = 8.7, P*C*H(CH$_3$)$_2$), 18.9 (vt, *N* = 7.7, P*C*H(CH$_3$)$_2$), 18.2 (s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6, 298 K): δ 38.1 (d, $^1J_{P-Rh}$ = 171.9).

Reaction of the mixture of Rh(C_6H_4-2-Cl){xant(P^iPr_2)$_2$} (20) and Rh(C_6H_3-2,3-Cl_2){xant(P^iPr_2)$_2$} (22) with HCl: Preparation of the mixture of RhHCl(C_6H_4-2-Cl){xant(P^iPr_2)$_2$} (19) and RhHCl(C_6H_3-2,3-Cl_2){xant(P^iPr_2)$_2$} (27). To a dark orange solution of the mixture of **20** and **22** (ratio 75: 25; 100 mg) was added dropwise a solution of HCl in toluene. The resulting solution was concentrated to dryness to afford a beige residue. Addition of pentane afforded a beige solid that was washed with pentane (3 x 1 mL). Yield: 79.4 mg. $^{31}P\{^1H\}$ NMR spectrum of this solid shows a mixture of RhHCl(C_6H_4-2-Cl){xant(P^iPr_2)$_2$} (**19**) and RhHCl(C_6H_3-2,3-Cl_2){xant(P^iPr_2)$_2$} (**27**) in a ratio 75:25.

*Spectroscopic data for RhHCl(C_6H_4-2-Cl){xant(P^iPr_2)$_2$} (**19**).* HRMS (electrospray, *m/z*) calcd. for $C_{33}H_{45}Cl_2OP_2Rh$ $[M]^+$: 691.1294; found 691.1243; calculated for $[M-Cl]^+$: 657.1684; found 657.1615. IR (cm^{-1}): ν(Rh-H) 2188 (w), ν(C=C) 1561 (m), ν(C-O-C) 1196 (m). ^1H NMR (300.13 MHz, C_6D_6, 298 K): δ 9.59 (d, J_{H-H} = 7.1, 1H, *o*-CH Ph), 7.41 (d, J_{H-H} = 7.1, 1H, *m*-CH Ph), 7.07 (dd, J_{H-H} = 7.1, J_{H-H} = 1.3, 2H, CH-arom POP), 7.04 (m, 2H CH-arom POP), 6.96 (dt, J_{H-H} = 7.0, J_{H-H} = 1.5, 1H, *m*-CH Ph), 6.86 (t, J_{H-H} = 7.6, 2H, CH-arom POP), 6.81 (t, J_{H-H} = 7.1, 1H, *p*-CH Ph), 2.68, 2.56 (both m, 2H, PC*H*(CH_3)$_2$), 1.63 (dvt, J_{H-H} = 7.3, *N* = 15.5, 6H, PCH(C*H*$_3$)$_2$), 1.29, 1.20 (both s, 3H, CH_3), 1.18 (dvt, J_{H-H} = 7.5, *N* = 15.9, 6H, PCH(C*H*$_3$)$_2$), 0.98 (dvt, J_{H-H} = 8.9, *N* = 16.2, 6H, PCH(C*H*$_3$)$_2$), 0.95 (dvt, J_{H-H} = 6.6, *N* = 13.5, 6H, PCH(C*H*$_3$)$_2$), -14.19 (dt, $^1J_{H-Rh}$ = 22.3, $^2J_{H-P}$ = 12.1, 1H, Rh-H). $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 298 K): δ 154.7 (vt, *N* = 9.7, Carom POP), 149.0 (dt, $^1J_{C-Rh}$ = 42.3, $^2J_{C-P}$ = 12.5, Rh-C Ph), 143.8 (s, *C*Cl Ph), 143.5 (s, CH Ph), 141.6 (s, CH Ph), 131.4 (s, Carom POP), 131.0 (s, CH-arom POP), 128.9 (s, CH-arom POP), 124.3 (s, CH Ph), 124.2 (s, CH Ph), 123.7 (s, CH-arom POP), 122.9 (vt, *N* = 25.4, Carom POP), 34.3 (s, C(*C*H$_3$)$_2$), 34.1 (s, C(*C*H$_3$)$_2$), 31.5 (s, *C*(CH$_3$)$_2$), 27.8 (vt, *N* = 25.9, P*C*H(CH$_3$)$_2$), 27.3 (vt, *N* = 21.9, P*C*H(CH$_3$)$_2$), 20.6, 18.9, 18.1, 17.4 (all s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 42.7 (d, $^1J_{P-Rh}$ = 112.7).

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with 1,3-dichlorobenzene: Preparation of RhHCl(C_6H_4-3-Cl){xant(P^iPr_2)$_2$} (23). A solution of **1** (100 mg, 0.18 mmol) was dissolved in pentane (5 mL) was treated with 1,3-dichlorobenzene (42 μL, 0.36 mmol) and the resulting mixture was stirred during 6 hours at room temperature. After this time, it was concentrated to dryness to afford a beige residue. Addition of pentane afforded a white solid that was washed with pentane (3 x 1 mL) and finally was dried in vacuo. Yield: 91.2 mg (72%). Anal. Calcd. for $C_{33}H_{45}Cl_2OP_2Rh$: C, 57.16; H, 6.54. Found: C, 56.91; H, 6.50. HRMS (electrospray, *m/z*) calcd. for $C_{33}H_{45}ClOP_2Rh$ $[M-Cl]^+$: 657.1684; found 657.1649. IR (cm^{-1}): ν(Rh-H) 2116 (w), ν(C=C) 1557 (m), ν(C-O-C) 1195 (m). ^1H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.44 (br, 2H, *o*-CH Ph), 7.21 (d, J_{H-H} = 13.16, 2H, CH-arom POP), 7.16 (m, 2H, CH-arom POP), 7.06 (d, J_{H-H} = 7.6, 1H, *p*-CH Ph), 6.99 (t, J_{H-H} = 7.5, 2H, CH-arom POP), 6.88 (t, J_{H-H} = 7.7, 1H, *m*-CH Ph), 2.79 (m, 2H, PC*H*(CH_3)$_2$), 2.30 (m, 2H, PC*H*(CH_3)$_2$), 1.58 (dvt, J_{H-H} = 7.4, *N* = 15.1, 6H, PCH(C*H*$_3$)$_2$), 1.38 (s, 3H, CH_3), 1.31 (dvt, J_{H-H} = 7.7, *N* = 15.7, 6H, PCH(C*H*$_3$)$_2$), 1.22 (s, 3H, CH_3), 1.09 (dvt, J_{H-H} = 7.7, *N* = 15.5, 6H, PCH(C*H*$_3$)$_2$), 1.01 (dvt, J_{H-H} = 7.4, *N* = 14.7, 6H, PCH(C*H*$_3$)$_2$), -16.04 (dt, $^1J_{H-Rh}$ = 25.9, $^2J_{H-P}$ = 12.8, 1H, Rh-H). $^{13}C\{^1H\}$ NMR (100.63 MHz, C_6D_6, 298 K): δ 155.3 (vt, *N* = 12.9, Carom POP), 147.7 (dt, $^1J_{C-Rh}$ = 36.6, $^2J_{C-P}$ = 10.1, Rh-C Ph), 132.1 (vt, *N* = 5.5, Carom POP), 131.3 (br, *C*Cl Ph) 130.8 (s, CH-arom POP), 128.3 (s, CH Ph), 126.9 (s, CH-arom POP), 124.7 (vt, *N* = 5.0, CH-arom POP), 123.7 (vt, *N* = 26.3, Carom POP), 121.5 (s, CH Ph), 34.5 (s, *C*(CH$_3$)$_2$), 34.0 (s, C(*C*H$_3$)$_2$), 28.9 (vt, *N* = 21.9, P*C*H(CH$_3$)$_2$), 28.6 (s, C(*C*H$_3$)$_2$), 27.4 (dvt, J_{C-Rh} = 2.7, *N* = 26.5, P*C*H(CH$_3$)$_2$), 20.8 (s, PCH(*C*H$_3$)$_2$), 19.0 (vt, *N* = 4.7, PCH(*C*H$_3$)$_2$), 18.9 (s, PCH(*C*H$_3$)$_2$), 18.7 (vt, *N* = 4.2, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6, 298 K): δ 41.1 (d, $^1J_{P-Rh}$ = 113.8).

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with 1,4-dichlorobenzene: Preparation of RhHCl(C_6H_4-4-Cl){xant(P^iPr_2)$_2$} (24). A solution of **1** (150 mg, 0.27 mmol) in pentane (5 mL) was treated with 1,4-dichlorobenzene was added (80 mg, 0.54 mmol) and the resulting mixture was stirred during 4 hours at room temperature. After this time, it was concentrated to dryness to afford a white residue. Addition of pentane afforded a beige solid that was washed with pentane (3 x 1 mL) and finally was dried in vacuo. Yield: 143.5 mg (75%). Anal. Calcd. for $C_{33}H_{45}Cl_2OP_2Rh$: C, 57.16; H, 6.54. Found: C, 56.97; H, 6.62. HRMS (electrospray, *m/z*) calcd. for $C_{33}H_{45}ClOP_2Rh$ $[M-Cl+H]^+$: 657.1684; found: 657.1706. IR (cm^{-1}): ν(Rh-H) 2098 (w), ν(C=C) 1549 (m), ν(C-O-C) 1192 (m). ^1H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.18 (br, 2H, *o*-CH Ph), 7.10 (d, J_{H-H} = 8.6, 2H, *m*-CH Ph), 7.06 (m, 2H, CH-arom POP), 7.05 (d, J_{H-H} = 7.6, 2H, CH-arom POP), 6.87 (t, J_{H-H} = 7.6, 2H, CH-arom POP), 2.71 (m, 2H, PC*H*(CH_3)$_2$), 2.19 (m, 2H, PC*H*(CH_3)$_2$), 1.53 (dvt, J_{H-H} = 7.3, *N* = 15.4, 6H, PCH(C*H*$_3$)$_2$), 1.28 (s, 3H, CH_3), 1.22 (dvt, J_{H-H} = 7.3, *N* = 16.2, 6H, PCH(C*H*$_3$)$_2$), 1.14 (s, 3H, CH_3), 0.99 (dvt, J_{H-H} = 7.8, *N* = 16.3, 6H, PCH(C*H*$_3$)$_2$), 0.95 (dvt, J_{H-H} = 7.7, *N* = 15.4, 6H, PCH(C*H*$_3$)$_2$), -15.66 (dt, $^1J_{H-Rh}$ = 26.1, $^2J_{H-P}$ = 13.0, 1H, Rh-H). $^{13}C\{^1H\}$ NMR (100.63 MHz, C_6D_6, 298 K): δ

155.0 (vt, N = 12.8, *C*arom POP), 142.7 (dt, $^{1}J_{C\text{-}Rh}$ = 38.2, $^{2}J_{C\text{-}P}$ = 10.0, Rh-C Ph), 132.1 (vt, N = 5.5, Carom POP), 130.8 (s, CH-arom POP), 128.4 (s, *C*Cl Ph) 128.5 (s, *m*-CH Ph), 126.1 (s, CH-arom POP), 124.7 (s, CH-arom POP), 123.8 (vt, N = 26.4, Carom POP), 34.5 (s, *C*(CH_3)$_2$), 34.1 (s, C(*C*H_3)$_2$), 28.9 (vt, N = 21.8, P*C*H(CH_3)$_2$), 28.6 (s, C(*C*H_3)$_2$), 27.4 (dvt, $J_{C\text{-}Rh}$ = 2.5, N = 26.4, P*C*H(CH_3)$_2$), 20.8 (s, PCH(*C*H_3)$_2$), 19.0 (vt, N = 4.7, PCH(*C*H_3)$_2$), 18.9 (s, PCH(*C*H_3)$_2$), 18.8 (vt, N = 4.1, PCH(*C*H_3)$_2$). $^{31}P\{^{1}H\}$ NMR (161.98 MHz, C_6D_6, 298 K): δ 41.2 (d, $^{1}J_{P\text{-}Rh}$ = 113.9).

Evolution of RhHCl(C_6H_4-3-Cl){xant(P^iPr_2)$_2$} (23) in acetone. A screwtop NMR tube charged with a solution of complex **23** (20 mg, 0.029 mmol) in acetone (0.4 mL) and it was periodically checked by $^{31}P\{^{1}H\}$ NMR spectroscopy. After 3 days at room temperature, the $^{31}P\{^{1}H\}$ NMR spectrum shows a mixture of RhHCl(C_6H_4-3-Cl){xant(P^iPr_2)$_2$} (**23**) and RhHCl(C_6H_4-4-Cl){xant(P^iPr_2)$_2$} (**24**) in a ratio 70:30.

Evolution of RhHCl(C_6H_4-4-Cl){xant(P^iPr_2)$_2$} (24) in acetone. A screwtop NMR tube charged with a solution of complex **24** (20 mg, 0.029 mmol) in acetone (0.4 mL) and it was periodically checked by $^{31}P\{^{1}H\}$ NMR spectroscopy. After 2 days at room temperature, the $^{31}P\{^{1}H\}$ NMR spectrum shows a mixture of RhHCl(C_6H_4-4-Cl){xant(P^iPr_2)$_2$} (**24**) and RhHCl(C_6H_4-3-Cl){xant(P^iPr_2)$_2$} (**23**) in a ratio 30:70.

Reaction of RhHCl(C_6H_4-3-Cl){xant(P^iPr_2)$_2$} (23) with with KO^{t}Bu: Preparation of Rh(C_6H_4-3-Cl){xant(P^iPr_2)$_2$} (25). This compound was prepared analogously as described for **4**, starting from **23** (100 mg, 0.14 mmol) and KO^{t}Bu (31 mg, 0.28 mmol), but stirring for 30 min. Orange solid. Yield: 89.2 mg (94%). Anal. Calcd. for $C_{33}H_{44}ClOP_2Rh$: C, 60.33; H, 6.75. Found: C, 59.88; H, 6.43. HRMS (electrospray, *m*/*z*) calcd. for $C_{33}H_{44}ClOP_2Rh$ $[M]^+$: 657.1684; found 657.1674. IR (cm^{-1}): ν(C=C) 1550 (m), ν(C-O-C) 1195 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.07 (t, $J_{H\text{-}P}$ = 1.8, 1H, *o*-CH Ph), 7.89 (dt, 1H, $J_{H\text{-}H}$ = 7.9, $J_{H\text{-}P}$ = 2.4, 1H, *o*-CH Ph), 7.22 (m, 2H, CH-arom POP), 7.01 (d, 2H, $J_{H\text{-}H}$ = 7.7, CH-arom POP), 6.96 (m, 2H, *m*-CH Ph and *p*-CH Ph), 6.83 (t, $J_{H\text{-}H}$ = 7.6, 2H, CH-arom POP), 2.33 (m, 4H, PC*H*(CH_3)$_2$), 1.21 (s, 6H, CH_3), 1.18 (dvt, $J_{H\text{-}H}$ = 7.3, N = 16.2, 12H, PCH(C*H*$_3$)$_2$), 1.12 (dvt, $J_{H\text{-}H}$ = 6.9, N = 14.0, 6H, PCH(C*H*$_3$)$_2$). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, C_6D_6, 298 K): δ 166.6 (dt, $^{1}J_{C\text{-}Rh}$ = 41.5, $^{2}J_{C\text{-}P}$ = 15.8, Rh-C Ph), 155.9 (vt, N = 15.8, Carom POP), 138.7 (s, *o*-CH Ph), 138.0 (s, *o*-CH Ph), 131.8 (s, *C*Cl Ph), 131.3 (s, CH-arom POP), 130.6 (s, Carom POP), 127.8 (s, CH-arom POP), 127.2 (s, CH Ph), 125.5 (vt, N = 14.2, Carom POP), 124.1 (s, CH-arom POP), 118.2 (s, CH Ph), 34.0 (s, *C*(CH_3)$_2$), 33.0 (s, C(*C*H_3)$_2$), 25.3 (vt, $J_{C\text{-}Rh}$ = 15.6, P*C*H(CH_3)$_2$), 19.3 (vt, N = 7.1, PCH(*C*H_3)$_2$), 18.6 (s, PCH(*C*H_3)$_2$). $^{31}P\{^{1}H\}$ NMR (161.98 MHz, C_6D_6, 298 K): δ 37.3 (d, $^{1}J_{P\text{-}Rh}$ = 173.3).

Reaction of RhHCl(C_6H_4-4-Cl){xant(P^iPr_2)$_2$} (24) with KO^{t}Bu: Preparation of Rh(C_6H_4-4-Cl){xant(P^iPr_2)$_2$} (26). This compound was prepared analogously as described for **4**, starting from **24** (100 mg, 0.14 mmol) and KO^{t}Bu (31 mg, 0.28 mmol), but stirring for 30 min at room temperature. Orange solid. Yield: 85.6 mg (90%). Anal. Calcd. for $C_{33}H_{44}ClOP_2Rh$: C, 60.33; H, 6.75. Found: C, 59.97; H, 6.62. HRMS (electrospray, *m*/*z*) calcd. for $C_{33}H_{44}Cl_2OP_2Rh$ $[M\text{-}Cl]^+$: 656.1605; found: 656.1619. IR (cm^{-1}): ν(C=C) 1594 (m), ν(C-O-C) 1190 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.88 (dd, $J_{H\text{-}H}$ = 8.2, $J_{H\text{-}P}$ = 2.2, 2H, *o*-CH Ph), 7.24 (d, $J_{H\text{-}H}$ = 8.2, 2H, *m*-CH Ph), 7.23 (m, 2H, CH-arom POP), 7.02 (d, $J_{H\text{-}H}$ = 7.7, 2H, CH-arom POP), 6.84 (t, $J_{H\text{-}H}$ = 7.6, 2H, CH-arom POP), 2.30 (m, 4H, PC*H*(CH_3)$_2$), 1.22 (s, 6H, CH_3), 115 (dvt, $J_{H\text{-}H}$ = 7.0, N = 15.8, 12H, PCH(C*H*$_3$)$_2$), 1.14 (dvt, $J_{H\text{-}H}$ = 6.8, N = 13.6, 6H, PCH(C*H*$_3$)$_2$). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, C_6D_6, 298 K): δ 160.6 (dt, $^{1}J_{C\text{-}Rh}$ = 41.3, $^{2}J_{C\text{-}P}$ = 13.9, Rh-C Ph), 156.2 (vt, N = 15.9, Carom POP), 140.6 (s, *o*-CH Ph), 131.3 (s, CH-arom POP), 130.8 (vt, N = 5.3, Carom POP), 127.8 (s, CH-arom POP), 125.6 (vt, N = 28.2, Carom POP), 125.3 (s, *m*-CH Ph), 124.3 (s, *C*Cl Ph), 124.1 (s, CH-arom POP), 34.0 (s, *C*(CH_3)$_2$), 33.0 (s, C(*C*H_3)$_2$), 25.3 (vt, N = 30.6, P*C*H(CH_3)$_2$), 19.4 (vt, N = 7.91, PCH(*C*H_3)$_2$), 18.9 (s, PCH(*C*H_3)$_2$). $^{31}P\{^{1}H\}$ NMR (161.98 MHz, C_6D_6, 298 K): δ 37.0 (d, $^{1}J_{P\text{-}Rh}$ = 174.0).

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with 1,2,3-trichlorobenzene. A solution of **1** (100 mg, 0.18 mmol) in pentane (4 mL) was treated with 1,2,3-trichlorobenzene (33 mg, 0.18 mmol) and the resulting mixture was stirred during 24 hours at room temperature. After this time, the reaction was checked by $^{31}P\{^{1}H\}$ NMR spectroscopy, showing a mixture of RhHCl(C_6H_3-2,3-Cl_2){xant(P^iPr_2)$_2$} (**27**) and Rh(C_6H_3-2,3-Cl_2){xant(P^iPr_2)$_2$} (**22**) in a ratio 67:33.

Isolation of Rh(C_6H_3-2,3-Cl_2){xant(P^iPr_2)$_2$} (22). The resulting mixture of the reaction of **1** with 1,2,3-trichlorobenzene was evaporated to dryness and was dissolved in acetone (5 mL). To this solution KO^{t}Bu (30.8 mg, 0.28 mmol) was added, and it was stirred during 5 min at room temperature. After this time, it was concentrated to dryness to afford a red residue. Toluene (2 mL) was added, and the resulting suspension was filtered to remove the potassium salts, getting a red solution, that was evaporated to dryness. Addition of pentane (3 mL) afforded a red solid, that was washed with pentane (3 x 1 mL) and finally, it was dried in vacuo. Yield: 112.5 mg (89%). Anal. Calcd. for $C_{33}H_{43}Cl_2OP_2Rh$: C, 57.32; H, 6.27. Found: C, 57.01; H, 5.95. HRMS (electrospray, *m*/*z*) calcd. for $C_{33}H_{43}Cl_2OP_2Rh$ $[M]^+$: 690.1216; found 690.1189. IR (cm^{-1}): ν(C=C) 1543 (m), ν(C-O-C) 1190 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.78 (dt, $J_{H\text{-}H}$ = 7.6, $J_{H\text{-}P}$ = 2.2,1H, *o*-CH), 7.16 (m, 2H CH-arom POP), 7.04 (d, $J_{H\text{-}H}$ = 7.6, 1H, *p*-CH Ph), 7.00 (dd, $J_{H\text{-}H}$ = 7.7, $J_{H\text{-}H}$ = 1.4, 2H, CH-arom POP), 6.80 (t, $J_{H\text{-}H}$ = 7.6, 2H, CH-arom POP), 6.74 (t, $J_{H\text{-}H}$ = 7.6, 1H, *m*-CH Ph), 2.34 (m, 4H, PC*H*(CH_3)$_2$), 1.26-1.02 (m, 30H, CH_3 + PCH(C*H*$_3$)$_2$). $^{13}C\{^{1}H\}$ NMR (100.62 MHz, C_6D_6, 298 K): δ 166.9 (dt, $^{1}J_{C\text{-}Rh}$ = 44.4, $^{2}J_{C\text{-}P}$ = 12.7, Rh-C Ph), 156.5 (vt, N =15.9, Carom POP), 139.9 (s, *o*-*C*H Ph), 139.7 (s, *C*-Cl Ph), 131.1 (s, *C*-Cl Ph), 130.9 (s, *C*H-arom POP), 130.0 (s, Carom POP), 127.8 (s, CH-arom POP), 125.0 (vt, N = 15.3, *C*arom POP), 124.3 (s, CH-arom POP), 123.8 (s, *m*-*C*H Ph), 120.9 (s, *p*-*C*H Ph), 35.0 (s, C(*C*H_3)$_2$), 34.1 (s, *C*(CH_3)$_2$), 30.0 (s, C(*C*H_3)$_2$), 26.4 (vt, N = 17.5, P*C*H(CH_3)$_2$), 24.3 (dvt, $J_{C\text{-}Rh}$ = 3.1, N = 18.2, P*C*H(CH_3)$_2$), 18.9 (vt, N = 7.5, P*C*H(CH_3)$_2$), 18.8 (vt, N = 7.4, P*C*H(CH_3)$_2$), 18.1 (s, PCH(*C*H_3)$_2$). $^{31}P\{^{1}H\}$ NMR (121.48 MHz, C_6D_6, 298 K): δ 38.4 (d, $^{1}J_{P\text{-}Rh}$ = 170.4).

Reaction of Rh(C_6H_3-2,3-Cl_2){xant(P^iPr_2)$_2$} (22) with HCl: Preparation of RhHCl(C_6H_3-2,3-Cl_2){xant(P^iPr_2)$_2$} (27). To a dark orange solution of **22** (100 mg, 0.14 mmol) in toluene (5 mL) was added dropwise a solution of HCl in toluene (1.5 mL, 0.25 M). The resulting beige solution was concentrated to dryness to afford a beige residue. Addition of pentane afforded a beige solid that was washed with pentane (3 x 1 mL) and finally it was dried in vacuo. Yield: 91 mg (86%). Anal. Calcd. for $C_{33}H_{44}Cl_3OP_2Rh$: C, 54.45; H, 6.09. Found: C, 54.08; H, 6.41. HRMS (electrospray, *m*/*z*) calcd.

for $C_{33}H_{44}Cl_2OP_2Rh$ $[M\text{-}Cl]^+$ 691.1294; found 691.1343. IR (cm^{-1}): ν(RhH) 2205 (w), ν(C=C) 1552 (m), ν(C-O-C) 1196 (m). ^1H NMR (300.13 MHz, C_6D_6, 298 K): δ 9.52 (d, $J_{H\text{-}H}$ = 8.0, 1H, *o*-CH Ph), 7.10 (dt, $J_{H\text{-}H}$ = 8.0, $J_{H\text{-}P}$ = 1.5, 1H, *p*-CH Ph), 7.04 (dd, $J_{H\text{-}H}$ = 7.7, $J_{H\text{-}H}$ = 1.3, 2H, CH-arom POP), 7.00 (m, 2H CH-arom POP), 6.89 (t, $J_{H\text{-}H}$ = 7.6, 2H, CH-arom POP), 6.72 (t, $J_{H\text{-}H}$ = 7.0, 1H, *m*-CH Ph), 2.65, 2.47 (both m, 2H, PC*H*$(CH_3)_2$), 1.59 (dvt, $J_{H\text{-}H}$ = 7.4, *N* = 15.6, 6H, PCH(C*H*$_3)_2$), 1.27, 1.18 (both s, 3H, CH_3), 1.12 (dvt, $J_{H\text{-}H}$ = 7.3, *N* = 16.6, 6H, PCH(C*H*$_3)_2$), 0.93 (dvt, $J_{H\text{-}H}$ = 7.3, *N* = 17.0, 6H, PCH(C*H*$_3)_2$), 0.91 (dvt, $J_{H\text{-}H}$ = 7.1, *N* = 13.9, 6H, PCH(C*H*$_3)_2$), -14.13 (dt, $^1J_{H\text{-}Rh}$ = 21.5, $J_{H\text{-}P}$ = 11.8, 1H, Rh-H). $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 298 K): δ 154.7 (vt, *N* = 12.5, Carom POP), 149.1 (dt, $^1J_{C\text{-}Rh}$ = 41.9, $^2J_{C\text{-}P}$ = 11.6, Rh-C Ph), 141.6 (s, *o*-CH Ph), 140.3 (vt, $J_{C\text{-}P}$ = 3.1, *o*-*C*Cl Ph), 131.4 (vt, *N* = 5.1, Carom POP), 131.0 (s, CH-arom POP), 130.7 (s, *m*-*C*Cl Ph), 129.0 (s, CH-arom POP), 124.8 (s, *p*-CH Ph), 124.5 (s, *m*-CH Ph), 124.4 (s, CH-arom POP), 122.5 (vt, *N* = 26.4, *C*arom POP), 34.2 (s, C(*C*$H_3)_2$), 31.4 (s, C(*C*$H_3)_2$), 30.2 (s, *C*$(CH_3)_2$), 27.8 (dvt, $J_{C\text{-}Rh}$ = 2.6, *N* = 26.6, P*C*H$(CH_3)_2$), 27.2 (vt, *N* = 22.5, P*C*H$(CH_3)_2$), 20.5 (s, PCH(*C*$H_3)_2$), 18.8 (s, PCH(*C*$H_3)_2$), 18.0 (vt, *N* = 5.5, PCH(*C*$H_3)_2$), 17.2 (s, PCH(*C*$H_3)_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 48.0 (d, $^1J_{P\text{-}Rh}$ = 111.7).

Reaction of RhH{xant(P^{i}Pr$_2$)$_2$} (1) with 1,2,4-trichlorobenzene: Preparation of RhHCl(C_6H_3-3,4-Cl_2){xant(P^{i}Pr$_2$)$_2$} (28). A solution of **1** (150 mg, 0.27 mmol) in pentane (5 mL) was treated with 1,2,4-trichlorobenzene (68 μL, 0.54 mmol) and the resulting mixture was stirred during 15 min at room temperature. After this time, it was concentrated to dryness to afford a beige residue. Addition of pentane afforded a beige solid that was washed with pentane (3 x 1 mL) and finally it was dried in vacuo. Yield: 123 mg (61.5%). Anal. Calcd. for $C_{33}H_{44}Cl_3OP_2Rh$: C, 54.45; H, 6.09. Found: C, 54.14; H, 6.33. HRMS (electrospray, *m*/*z*) calcd. for $C_{33}H_{44}Cl_2OP_2Rh$ $[M\text{-}Cl]^+$: 691.1294; found 691.1351. IR (cm^{-1}): ν(Rh-H) 2102 (w), ν(C=C) 1540 (w), ν(C-O-C) 1194 (m). ^1H NMR (400.13 MHz, C_6D_6, 298 K): δ 8.26 (br, 2H, *o*-CH Ph), 7.07 (d, $J_{H\text{-}H}$ = 8.4, 1H, *p*-CH Ph), 7.02 (dd, $J_{H\text{-}H}$ = 7.5, $J_{H\text{-}H}$ = 1.3, 2H, CH-arom POP), 7.01 (m, 2H, CH-arom POP), 6.85 (t, $J_{H\text{-}H}$ = 7.6, 2H, CH-arom POP), 2.66 (m, 2H, PC*H*$(CH_3)_2$), 2.14 (m, 2H, PC*H*$(CH_3)_2$), 1.48 (dvt, $J_{H\text{-}H}$ = 7.3, *N* = 15.7, 6H, PCH(C*H*$_3)_2$), 1.26 (s, 3H, CH_3), 1.20 (dvt, $J_{H\text{-}H}$ = 7.2, *N* = 16.4, 6H, PCH(C*H*$_3)_2$), 1.12 (s, 3H, CH_3), 0.95 (dvt, $J_{H\text{-}H}$ = 8.6, *N* = 17.2, 6H, PCH(C*H*$_3)_2$), 0.90 (dvt, $J_{H\text{-}H}$ = 7.6, *N* = 15.6, 6H, PCH(C*H*$_3)_2$), -15.59 (dt, $^1J_{H\text{-}Rh}$ = 25.8, $^2J_{H\text{-}P}$ = 12.9, 1H, Rh-H). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6, 298 K): δ 155.3 (vt, *N* = 13.4, Carom POP), 145.4 (dt, $^1J_{C\text{-}Rh}$ = 37.8, $^2J_{C\text{-}P}$ = 10.1, Rh-C Ph), 132.1 (vt, *N* = 5.2, Carom POP), 130.8 (s, CH-arom POP), 128.4 (s, *C*Cl Ph), 128.0 (s, CH-arom POP), 127.3 (s, *m*-CH Ph), 125.3 (s, *C*Cl Ph), 124.8 (vt, *N* = 5.3, CH-arom POP), 123.6 (vt, *N* = 26.7, Carom POP), 34.6 (s, *C*$(CH_3)_2$), 34.1 (s, C(*C*$H_3)_2$), 29.0 (vt, *N* = 22.3, P*C*H$(CH_3)_2$), 28.5 (s, C(*C*$H_3)_2$), 27.5 (dvt, $J_{C\text{-}Rh}$ = 2.4, *N* = 26.4, P*C*H$(CH_3)_2$), 20.8 (s, PCH(*C*$H_3)_2$), 19.0 (vt, *N* = 5.2, PCH(*C*$H_3)_2$), 19.0 (s, PCH(*C*$H_3)_2$), 18.7 (vt, *N* = 4.4, PCH(*C*$H_3)_2$). $^{31}P\{^1H\}$ NMR (121.48 MHz, C_6D_6, 298 K): δ 41.7 (d, $^1J_{P\text{-}Rh}$ = 111.7).

Reaction of RhH{xant(P^{i}Pr$_2$)$_2$} (1) with 1,3,5-trichlorobenzene: Preparation of RhHCl(C_6H_3-3,5-Cl_2){xant(P^{i}Pr$_2$)$_2$} (29). A solution of **1** (150 mg, 0.27 mmol) pentane (5 mL) was treated with 1,3,5-trichlorobenzene (100 mg, 0.54 mmol) and the resulting mixture was stirred during 5 min at room temperature. After this time, it was concentrated to dryness to afford a beige residue. Addition of pentane afforded a beige solid that was washed with pentane (3 x 1 mL) and finally it was dried in vacuo. Yield: 132.5 mg (63%). Anal. Calcd. for $C_{33}H_{44}Cl_3OP_2Rh$: C, 54.45; H, 6.09. Found: C, 54.30; H, 6.39. HRMS (electrospray, *m*/*z*) calcd. for $C_{33}H_{44}Cl_2OP_2Rh$ $[M\text{-}Cl]^+$: 691.1294; found: 691.1277. IR (cm^{-1}): ν(Rh-H) 2106 (w), ν(C=C) 1539 (m), ν(C-O-C) 1195 (m). ^1H NMR (400.13 MHz, C_6D_6, 298 K): δ 8.44 (br, 2H, *o*-CH Ph), 7.11 (s, 1H, *p*-CH Ph), 7.02 (dd, $J_{H\text{-}H}$ = 7.6, $J_{H\text{-}H}$ = 1.4, 2H, CH-arom POP), 6.99 (m, 2H, C*H*-arom POP), 6.84 (t, $J_{H\text{-}H}$ = 7.6, 2H, CH-arom POP), 2.66 (m, 2H, PC*H*$(CH_3)_2$), 2.15 (m, 2H, PC*H*$(CH_3)_2$), 1.46 (dvt, $J_{H\text{-}H}$ = 7.3, *N* = 15.7, 6H, PCH(C*H*$_3)_2$), 1.25 (s, 3H, CH_3), 1.21 (dvt, $J_{H\text{-}H}$ = 7.2, *N* = 16.4, 6H, PCH(C*H*$_3)_2$), 1.13 (s, 3H, CH_3), 0.99 (dvt, $J_{H\text{-}H}$ = 7.2, *N* = 15.8, 6H, PCH(C*H*$_3)_2$), 0.89 (dvt, $J_{H\text{-}H}$ = 7.1, *N* = 14.9, 6H, PCH(C*H*$_3)_2$), -15.53 (dt, $^1J_{H\text{-}Rh}$ = 25.5, $^2J_{H\text{-}P}$ = 12.7, 1H, Rh-H). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6, 298 K): δ 155.5 (vt, *N* = 12.8, *C*arom POP), 149.7 (dt, $^1J_{C\text{-}Rh}$ = 37.7, $^2J_{C\text{-}P}$ = 9.8, Rh-C Ph), 132.3 (vt, *N* = 5.5, Carom POP), 131.5 (s, *C*Cl Ph), 131.0 (s, CH-arom POP), 128.1 (s, CH-arom POP), 125.1 (vt, *N* = 5.2, CH-arom POP), 123.7 (vt, *N* = 26.9, Carom POP), 121.7 (s, *p*-CH Ph), 34.7 (s, *C*$(CH_3)_2$), 34.2 (s, C(*C*$H_3)_2$), 29.2 (vt, *N* = 22.3, P*C*H$(CH_3)_2$), 28.9 (s, C(*C*$H_3)_2$), 27.7 (dvt, $J_{C\text{-}Rh}$ = 2.7, *N* = 26.9, P*C*H$(CH_3)_2$), 20.9 (s, PCH(*C*$H_3)_2$), 19.2 (vt, *N* = 4.1, PCH(*C*$H_3)_2$), 19.2 (s, PCH(*C*$H_3)_2$), 18.9 (vt, *N* = 3.7, PCH(*C*$H_3)_2$). $^{31}P\{^1H\}$ NMR (121.48 MHz, C_6D_6, 298 K): δ 41.9 (d, $^1J_{P\text{-}Rh}$ = 111.2).

Reaction of RhHCl(C_6H_3-3,4-Cl_2){xant(P^{i}Pr$_2$)$_2$} (28) with KO^{t}Bu: Preparation of Rh(C_6H_3-3,4-Cl_2){xant(P^{i}Pr$_2$)$_2$} (30). This compound was prepared analogously as described for **4**, starting from **28** (100 mg, 0.14 mmol) and KO^{t}Bu (31 mg, 0.28 mmol), but stirring during 3 h at room temperature. Orange solid. Yield: 91.6 mg (95 %). Anal. Calcd. for $C_{33}H_{43}Cl_2OP_2Rh$: C, 57.32; H, 6.27. Found: C, 57.25; H, 6.13 HRMS (electrospray, *m*/*z*) calcd. for $C_{33}H_{43}Cl_2OP_2Rh$ $[M]^+$: 691.1294; found: 691.1293. IR (cm^{-1}): ν(C=C) 1530 (w), ν(C-O-C) 1191 (m). ^1H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.19 (s, 1H, *o*-CH Ph), 7.71 (dt, $J_{H\text{-}H}$ = 8.0, $J_{H\text{-}P}$ = 1.8, 1H, *o*-CH Ph), 7.16 (m, 3H, CH-arom POP + *m*-CH Ph), 6.98 (dd, $J_{H\text{-}H}$ = 7.6, $J_{H\text{-}H}$ = 1.5, 2H, CH-arom POP), 6.79 (t, $J_{H\text{-}H}$ = 7.6, 2H, CH-arom POP), 2.26 (m, 4H, PC*H*$(CH_3)_2$), 1.19 (s, 6H, CH_3), 1.11 (dvt, $J_{H\text{-}H}$ = 7.4, *N* = 16.5, 12H, PCH(C*H*$_3)_2$), 1.08 (dvt, $J_{H\text{-}H}$ = 7.1, *N* = 14.2, 12H, PCH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6, 298 K): δ 165.1 (dt, $^1J_{C\text{-}Rh}$ = 46.6, $^2J_{C\text{-}P}$ = 14.9, Rh-C Ph), 156.1 (vt, *N* = 15.9, *C*arom POP), 140.2 (s, *o*-CH Ph), 139.3 (s, *o*-CH Ph), 131.3 (s, CH-arom POP), 130.8 (vt, *N* = 5.4, Carom POP), 129.0 (s, *C*Cl Ph), 127.9 (s, CH-arom POP), 126.5 (s, *m*-CH Ph), 125.2 (vt, *N* = 16.4, Carom POP), 124.1 (s, CH-arom POP), 121.2 (s, C-Cl Ph), 34.0 (s, *C*$(CH_3)_2$), 33.0 (s, C(*C*$H_3)_2$), 25.4 (dvt, $J_{C\text{-}Rh}$ = 2.7, *N* = 18.4, P*C*H$(CH_3)_2$), 19.3 (vt, *N* = 8.1, P*C*H$(CH_3)_2$), 18.5 (s, PCH(*C*$H_3)_2$). $^{31}P\{^1H\}$ NMR (121.48 MHz, C_6D_6, 298 K): δ 37.7 (d, $^1J_{P\text{-}Rh}$ = 171.3).

Reaction of RhHCl(C_6H_3-3,5-Cl_2){xant(P^{i}Pr$_2$)$_2$} (29) with KO^{t}Bu: Preparation of Rh(C_6H_3-3,5-Cl_2){xant(P^{i}Pr$_2$)$_2$} (31). This compound was prepared analogously as described for **4**, starting from **29** (100 mg, 0.14 mmol) and KO^{t}Bu (31 mg, 0.28 mmol), but stirring during 3 h at room temperature. Orange solid. Yield: 86.5 mg (91%). Anal. Calcd. for $C_{33}H_{43}Cl_2OP_2Rh$: C, 57.32; H, 6.27. Found: C, 57.67; H, 5.89. HRMS (electrospray, *m*/*z*): calcd. for $C_{33}H_{43}Cl_2OP_2Rh$ $[M]^+$: 690.1217; found 690.1216. IR (cm^{-1}):

ν(C=C) 1525 (m), ν(C-O-C) 1197 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.05 (t, J_{H-P} = 2.4, 2H, *o*-CH Ph), 7.16 (m, 2H, CH-arom POP), 7.06 (s, 1H, *p*-CH Ph), 6.99 (dd, J_{H-H} = 7.7, J_{H-H} = 1.2, 2H, CH-arom POP), 6.80 (t, J_{H-H} = 7.7, 2H, CH-arom POP), 2.26 (m, 4H, PC*H*$(CH_3)_2$), 1.17 (s, 6H, CH_3), 1.13 (dvt, J_{H-H} = 8.8, *N* = 16.6, 12H, PCH(C*H*$_3)_2$), 1.05 (dvt, J_{H-H} = 7.0, *N* = 14.0, 12H, PCH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (75.45 MHz, C_6D_6, 298 K): δ 170.7 (dt, $^1J_{C-Rh}$ = 42.5, $^2J_{C-P}$ = 12.5, Rh-C Ph), 156.1 (vt, *N* = 16.7, Carom POP), 137.0 (t, J_{C-P} = 2.8, *o*-CH Ph), 131.4 (s, *C*-Cl Ph), 131.1 (s, CH-arom POP), 130.8 (vt, *N* = 5.4, Carom POP), 127.9 (s, CH-arom POP), 124.9 (vt, *N* = 17.6, Carom POP), 124.2 (s, CH-arom POP), 117.9 (s, *p*-CH Ph), 34.0 (s, *C*$(CH_3)_2$), 32.9 (s, C(*C*H$_3)_2$), 25.3 (dvt, J_{C-Rh} = 2.6, *N* = 18.6, P*C*H$(CH_3)_2$), 19.2 (vt, *N* = 8.0, P*C*H$(CH_3)_2$), 18.5 (s, PCH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (121.48 MHz, C_6D_6, 298 K): δ 38.1 (d, $^1J_{P-Rh}$ = 170.0).

Structural Analysis of Complexes 2, 17, 25, 27 and 29. X-ray data were collected on a Bruker Smart APEX CCD (**25**) or APEX CCD DUO (**2**, **27** and **29**) or Oxford Diffraction XcaliburTS (**17**). Data were collected using monochromated Mo Kα radiation (λ = 0.71073) in the ω-scan mode. The crystals were mounted in inert oil on a glass fiber and transferred to the cold gas stream of the corresponding diffractometer. Data were collected over the complete sphere and were corrected for absorption by using a multiscan method applying the CrisAlys RED package[30] for complex **17**, and the SADABS program for the other ones.[31] The structures were solved by Patterson or direct methods and refined by full-matrix least squares on F^2 with SHELXL97,[32] including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms (except hydrides) were observed in the least Fourier Maps or calculated, and refined freely or using a restricted riding model. The hydrogen atoms bonded to the rhodium atoms were observed in the last cycles of refinement but refined too close to the metal, so a restricted refinement model was used for all of them (d(Rh-H= 1.59(1) Å) (**2**, **27**, **29**).

Crystal data for **2**: $C_{33}H_{46}ClOP_2Rh$, M_W 659.00, yellow, irregular block (0.15 x 0.12 x 0.06), monoclinic, space group $P2_1/n$, *a*: 9.481(2) Å, *b*: 19.524(5) Å, *c*: 17.101(4) Å, *β*: 91.465(4)°, *V* = 3164.6(13) Å^3, *Z* = 4,*Z'* = 1, D_{calc}: 1.383 g cm^{-3}, F(000): 1376, T = 100(2) K, μ 0.749 mm^{-1}. 33568 measured reflections (2θ: 3-58°, ω scans 0.3°), 8151 unique (R_{int} = 0.0909); min./max. transm. factors 0.404/0.862. Final agreement factors were R^1 = 0.0503 (5280 observed reflections, I > 2σ(I)) and wR^2 = 0.1208; data/restraints/parameters 8151/3/356; GoF = 1.006. Largest peak and hole 0.837 (close to rhodium atom) and -1.072 e/ Å^3.

Crystal data for **17**: $C_{33}H_{44}FOP_2Rh$, M_W 640.53, orange, plate (0.33 x 0.20 x 0.05), orthorhombic, space group Pbca, *a*: 14.6602(4) Å, *b*: 20.0564(7) Å, *c*: 21.1865(8)Å, *V* = 6229.5(4) Å^3, *Z* = 8, *Z'* = 1, D_{calc}: 1.366g cm^{-3}, F(000): 2672, T = 150(2) K, μ 0.681 mm^{-1}. 25162 measured reflections (2θ: 3-51°), 6601 unique (R_{int} = 0.0918); min./max. transm. factors 0.94/1.0. Final agreement factors were R^1 = 0.0532 (3787 observed reflections, I > 2σ(I)) and wR^2 = 0.1084; data/restraints/parameters 6601/0/353; GoF = 1.027. Largest peak and hole 0.770 (close to rhodium atoms) and -0.746 e/ Å^3.

Crystal data for **25**: $C_{33}H_{44}ClOP_2Rh$, M_W 656.98, red, irregular block (0.19 x 0.15 x 0.13), orthorhombic, space group Pbca, *a*: 14.7544(11) Å, *b*: 19.8932(16) Å, *c*: 21.5065(17) Å, *V* = 6312.4(9) Å^3, *Z* = 8, *Z'* = 1, D_{calc}: 1.383 g cm^{-3}, F(000): 2736, T = 100(2) K, μ 0.751 mm^{-1}. 56321 measured reflections (2θ: 3-57°, ω scans 0.3°), 7732 unique (R_{int} = 0.0968); min./max. transm. factors 0.760/0.862. Final agreement factors were R^1 = 0.0479 (5300 observed reflections, I > 2σ(I)) and wR^2 = 0.0948; data/restraints/parameters 7732/0/353; GoF = 1.037. Largest peak and hole 0.577 (close to rhodium atom) and -0.622 e/ Å^3.

Crystal data for **27**: $C_{33}H_{44}Cl_3OP_2Rh$, M_W 727.88, orange, irregular block (0.18 x 0.11 x 0.10), monoclinic, space group $P2_1/n$, *a*: 11.854(3) Å, *b*: 23.722(6) Å, *c*: 12.685(3) Å, *β*: 112.216(4)°, *V* = 3302.3(14) Å^3, *Z* = 4, *Z'* = 1, D_{calc}: 1.464g cm^{-3}, F(000): 1504, T = 100(2) K, μ 0.882 mm^{-1}. 26023 measured reflections (2θ: 3-58°, ω scans 0.3°), 6036 unique (R_{int} = 0.1345); min./max. transm. factors 0.691/0.862. Final agreement factors were R^1 = 0.0579 (3498 observed reflections, I > 2σ(I)) and wR^2 = 0.1520; data/restraints/parameters 6036/8/373; GoF = 1.029. Largest peak and hole 1.064(close to rhodium atom) and -0.661 e/ Å^3.

Crystal data for **29**: $C_{33}H_{44}Cl_3OP_2Rh$, 0.5x(C_3H_6O), M_W 756.92, yellow, irregular block (0.30 x 0.03 x 0.03), monoclinic, space group C2/c, *a*: 47.708(8) Å, *b*: 12.228(2) Å, *c*: 33.505(5) Å, *β*: 133.874(2)°, *V* = 14090(4) Å^3, *Z* = 16, *Z'* = 2, D_{calc}: 1.427 g cm^{-3}, F(000): 6272, T = 173(2) K, μ 0.831 mm^{-1}. 26023 measured reflections (2θ: 3-52°, ω scans 0.3°), 73659 unique (R_{int} = 0.0558); min./max. transm. factors 0.712/0.862. Final agreement factors were R^1 = 0.0622 (14347 observed reflections, I > 2 σ(I)) and wR^2 = 0.1613; data/restraints/parameters 18293/2/779; GoF = 1.113. Largest peak and hole 2.611 (close to rhodium atom) and -0.822 e/ Å^3.

ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR data of complexes **2**, **5**, **6**, **9**, **10**, **13**, **23**, **24**, **28** and **29** in acetone-d_6, details on the calculation of the rotational barriers of the aryl groups, preparation of RhHBr(C_6H_5){xant(P^iPr_2)$_2$} and ^{1}H and ^{31}P{^{1}H} NMR spectra of the new complexes. CIF files giving positional and displacement parameters, crystallographic data, and bond lengths and angles of compounds **2**, **17**, **25**, **27** and **29**. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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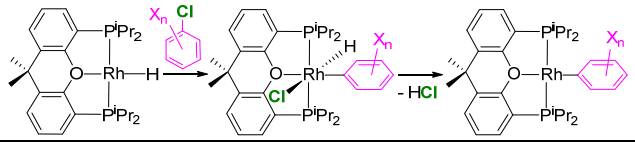
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