Reactions of POP-Pincer Rhodium(I)-Aryl Complexes with Small Molecules: Coordination Flexibility of the Ether Diphosphine

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Abstract: Reactions of the aryl complexes Rh(aryl){κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**1**; aryl = 3,5-$Me_2C_6H_3$ (**a**), C_6H_5 (**b**), 3,5-$Cl_2C_6H_3$ (**c**), 3-FC_6H_4 (**d**); xant(P^{i}Pr$_2$)$_2$ = 9,9-dimethyl-4,5-bis-(diisopropylphosphino)xanthene) with O_2, CO, and $MeO_2CC{\equiv}CCO_2Me$ have been performed. Under 1 atm of O_2, the pentane solutions of complexes **1** afford the dinuclear peroxide derivatives [Rh(aryl){κ^2-P,P-xant(P^{i}Pr$_2$)$_2$}]$_2$(μ-O_2)$_2$ (**2**a-**d**) as yellow solids. In solution these species are unstable. In dichloromethane, at room temperature they are transformed into the dioxygen adducts Rh(aryl)(η^2-O_2){κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**3a-d**), as a result of the rupture of the double peroxide bridge and the reduction of the metal center. Complex **3b** decomposes in benzene, at 50 ºC, to give diphosphine oxide, phenol and biphenyl. Complexes **1** react with CO to give the square-planar mono carbonyl derivatives Rh(aryl)(CO){κ^2-P,P-[xant(P^{i}Pr$_2$)$_2$]} (**4a-d**), which under carbon monoxide atmosphere evolve to benzoyl species Rh{C(O)aryl}(CO){κ^2-P,P-[xant(P^{i}Pr$_2$)$_2$]} (**5a-d**), resulting from the migratory insertion of CO into the Rh-aryl bond and the coordination of a second CO molecule. The transformation is reversible; under vacuum, complexes **5** regenerate the precursors **4**. The addition of the activated alkyne to complexes **1b** and **1d** initially leads to the π-alkyne intermediates Rh(aryl){η^2-C(CO_2Me)≡C(CO_2Me)}{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**6b**, **6d**) which evolve to the alkenyl derivatives Rh{*(E)*-C(CO_2Me)=C(CO_2Me)aryl}{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**7b**, **7d**). The diphosphine adapts its coordination mode to the stability requirements of the different complexes, coordinating *cis*-κ^2-P,P in complexes **2**, *fac*-κ^3-P,O,P in compounds **3**, *trans*-κ^2-P,P in the mono carbonyl derivatives **4** and **5**, and *mer*-κ^3-P,O,P in products **6** and **7**.

Key words: Rhodium; pincer ligand; peroxide; carbonyl; aryl

Introduction

Square-planar rhodium(I) aryl complexes of general formula L_3Rh-aryl are stabilized with three phosphines,[1] bulky carbenes,[2] or bulky substituents at the *ortho* positions of the coordinated aryl group.[3] From an electronic point of view, the carbonyl ligand[4] and fluorine substituents at the aryl group[1c,e;2a,b;4c;5] also appear to increase the stability of these compounds. As a consequence of the limited number of species isolated, the studies on stoichiometric reactivity are very scarce, being focused on the protolytic cleavage of the Rh-C bond[4a] and insertion reactions into the latter of cumulenes,[1a] aldehydes,[4b] ketones,[6] alkynones,[6a] imines,[6a,7] and nitriles.[6b]

Two families of pincer ligands have been mainly used to stabilize square-planar complexes of formula L_3Rh-aryl: P,N,P-ligands based on 2,6-bis(dialkylphosphinomethyl)pyridines[8] and flexible P,O,P-groups.[9] The deprotonation of one of the CH_2 arms of the first ones gives rise to the dearomatization of the pyridine ring. This facilitates processes of activation of aromatic C-H bonds, which leads to rhodium(I)-aryl derivatives regenerating the initial ligand (Scheme 1).[8e,f,h,j] On the other hand, it has been shown that the hydride complex RhH{κ^3-P,O,P-[xant($P^iPr_2)_2$]} (xant($P^iPr_2)_2$ = 9,9-dimethyl-4,5-bis-(diisopropylphosphino)xanthene) oxidatively adds aromatic C-H and C-Cl bonds to give the rhodium(III) species RhH_2(aryl){κ^3-P,O,P-[xant($P^iPr_2)_2$]} and RhH(aryl)Cl{κ^3-P,O,P-[xant($P^iPr_2)_2$]}. In spite of the *trans* disposition of the hydrides in the first ones and the hydride and chloride in the second ones, the flexibility of the P,O,P ligand allows the reductive elimination of H_2 and HCl, respectively, which leads to a wide variety of square-planar Rh(aryl){κ^3-P,O,P-[xant($P^iPr_2)_2$]} complexes (Scheme 2).[9a,c,d] Both families show interesting catalytic uses; P,N,P-rhodium(I)-aryl derivatives promote the catalytic deuteration of arenes,[8c,d] in addition to cross-coupling of aryl iodides with sp^2 and sp^3 C-H bonds,[8h] whereas the

P,O,P-aryl complexes Rh(aryl){κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} are the key intermediates in the direct borylation of arenes[9a] and in the decyanative borylation of aryl nitriles.[9b] These uses indicate that square-planar L_3Rh-aryl complexes bearing L_3-pincer ligands can play a notable role in the direct functionalization of arenes.[10]

[Insert Scheme 1 here]

[Insert Scheme 2 here]

Our interest in the chemistry of platinum group metal complexes with P,O,P-pincer ligands[9a-c;11] and in the direct functionalization of hydrocarbons[12] prompted us to study model reactions of complexes Rh(aryl){κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} with three different molecules: oxygen, carbon monoxide, and dimethyl acetylenedicarboxylate. These reactions are relevant by their connection with three catalytic processes for the direct functionalization of arenes: oxidation to phenols,[13] carbonylation to benzaldehydes,[14] and vinylation to styrenes.[15] This paper shows the interaction of these molecules with the metal center of the aryl complexes, the influence of the molecules coordination in the coordination mode of the diphosphine, and their ability to insert into the Rh-aryl bond.

Results and discussion

Reactions with molecular oxygen

The unsaturated rhodium center of the aryl complexes Rh(aryl){κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (**1**; aryl = 3,5-$Me_2C_6H_3$ (**a**), C_6H_5 (**b**), 3,5-$Cl_2C_6H_3$ (**c**), 3-FC_6H_4 (**d**)) coordinates molecular oxygen. Stirring of pentane solutions of **1** under 1 atm of this gas, or exposed to air, at room temperature affords yellow solids of formula $[Rh(aryl)(O_2)\{xant(P^iPr_2)_2\}]_x$ (**2**), according to their C,H elemental analysis, in almost quantitative yield (87-93%).

The X-ray diffraction analysis structure (Figure 1) of the 3,5-$Me_2C_6H_3$-derivative **2a** reveals that these compounds are dinuclear species (x = 2), which have an inversion center. Two oxygen molecules bond the rhodium centers of two $Rh(aryl)\{xant(P^iPr_2)_2\}$ metal fragments, forming a double μ-κ^1:η^2 peroxide bridge (O(1)-O(2) = O(1A)-O(2A) = 1.442(5) Å). The coordination of the oxygen molecules to the rhodium centers is asymmetric displaying three different metal-oxygen bond lengths: Rh-O(1) = Rh(A)-O(1A) = 1.988(4) Å, Rh(A)-O(2) = Rh-O(2A) = 2.024(4) Å, and Rh-O(2) = Rh(A)-O(2A) = 2.439(3) Å. The dimeric nature of these species is noticeable, since comparable reactions usually lead to mononuclear derivatives. The Cambridge Structural Database (2019 version; update 3) contains 51 structures bearing the RhO_2 unit. From them, 48 correspond to mononuclear species, 36 are peroxide derivatives (1.41-1.46 Å)[16,17] and 12 are dioxygen adducts (1.27-1.39 Å);[17,18] a structure related to that shown in Figure 1 has been previously reported only in three cases: $[RhCl(PPh_3)_2]_2(\mu\text{-}O_2)_2$,[19] $[Rh(PhBP_3)]_2(\mu\text{-}O_2)_2$ ($PhBP_3$ = tris(methylenediphenylphosphane)phenylborate),[20] and $[Rh\{(E)\text{-}CF{=}CF(CF_3)\}(PEt_3)_2]_2(\mu\text{-}O_2)_2$.[21] This dimeric structure is rare not only in the rhodium chemistry, but also for the platinum group metals. As far as we know, the palladium complex $[Pd(\kappa^2\text{-}Tp^{iPr2})(py)]_2(\mu\text{-}O_2)$ (Tp^{iPr2} = hydridotris(3,5-diisopropylpyrazolyl)borate) is the other precedent, between the remaining platinum group metals, although it only bears a single peroxide bridge.[22]

[Insert Figure 1 here]

The structure shown in Figure 1 also reveals that during the oxidation of complexes **1** (Scheme 3), the coordination mode of the diphosphine changes from *mer*-κ^3-P,O,P to *cis*-κ^2-P,P, decreasing the P-Rh-P angle to 103.59(5)º. The change prevents the steric hindrance that the isopropyl substituents should undergo in a *mer*-κ^3-P,O,P coordination of the diphosphine in a dimeric structure. A similar phenomenon has been previously observed during the formation of the dinuclear cation $[(Os(H\cdots H)\{\kappa^3\text{-P,O,P-xant}(P^iPr_2)_2\})_2(\mu\text{-Cl})_2]^{2+}$, which contains a *fac*-coordinated κ^3-P,O,P diphosphine. The flexibility of the xanthene linker certainly favors the change.[23]

[Insert Scheme 3 here]

The coordination polyhedron around the rhodium atoms of these $[Rh(aryl)\{\kappa^2\text{-P,P-xant}(P^iPr_2)_2\}]_2(\mu\text{-}O_2)_2$ (**2**; aryl = 3,5-$Me_2C_6H_3$ (**a**), C_6H_5 (**b**), 3,5-$Cl_2C_6H_3$ (**c**), 3-FC_6H_4 (**d**)) complexes can be rationalized as the distorted octahedron expected for rhodium(III) centers, with the oxygen atoms disposed *fac*, and the aryl group situated *pseudo-trans* to the longest Rh-O bond (C(1)-Rh-O(2) = C(1A)-Rh(A)-O(2A) = 132.37(17)º).

The double bridge is broken in solution at room temperature (Scheme 4). The cleavage is strongly supported by ^{1}H NMR Diffusion-ordered spectroscopy (^{1}H-DOSY) experiments in dichloromethane. Pulse field gradient (PFG) NMR is a method for measuring diffusion rates of molecules in solution, which depends on their size and hydrodynamic volume.[24] Table 1 shows that the diffusion coefficients obtained from the dichloromethane solutions of **2b-d** and the respective calculated hydrodynamic radii are similar to those of the corresponding precursors **1b-d.** The rupture also occurs in other solvents such as acetonitrile. The electrotrospray HRM spectra of **2a-d** in the latter display molecular peaks corresponding to monomeric species; i.e., a half of the expected ones for the dinuclear complexes. This is in contrast to that observed for the previously reported compounds $[Rh(PhBP_3)]_2(\mu\text{-}O_2)_2$ and $[Rh\{(E)\text{-}CF{=}CF(CF_3)\}(PEt_3)_2]_2(\mu\text{-}O_2)_2$, which kept their dinuclear structure in solution.[20,21]

[Insert Scheme 4 here]

The $^{31}P\{^1H\}$ NMR spectra in dichloromethane solutions of the four oxidized species display doublets at about 40 ppm, suggesting equivalent P^iPr_2 groups, which is not consistent with the structure shown in Figure 1. Furthermore, the values of P-Rh coupling constants between 147 and 155 Hz are outside the range of Rh-P coupling constants observed for rhodium(III) complexes bearing the xant$(P^iPr_2)_2$ diphosphine (86-132 Hz),[9a-c;25] while they lie in that reported for the derivatives of rhodium(I) with this diphosphine (140-198 Hz).[9a,c;25a,b;26] This reveals that the rupture of the double peroxide bridge produces the reduction of the metal centers, which must imply a peroxide-to-dioxo transformation. According to this, the IR spectra in CCl_4 contain a characteristic dioxo ν(O-O) band[17a] at 1064 cm^{-1}, which is absent in solid state.

The equivalence of the P^iPr_2 groups along with the presence of four doublet of doublets between 1.4 and 0.8 ppm, corresponding to the methyl groups of the isopropyl substituents, in the ^1H NMR spectra point out a *fac*-κ^3-P,O,P coordination of the diphosphine.[27] So, the coordination polyhedron of the oxidized species in solution appears to be a trigonal bipyramid[28] with the oxygen atom of the diphosphine and the phenyl group in apical positions, while the dioxygen ligand and the phosphorous atoms should lie in the equatorial plane.[29] On the basis of this structure, the reduction process can be understood as a sequential rupture of the Rh-O bonds following an inverse relationship to their strength.

The dinuclear complexes **2a-d** are stable in the solid state, under argon, at room temperature for long time. In contrast, the mononuclear species $Rh(aryl)(\eta^2\text{-}O_2)\{\kappa^3\text{-}P,O,P\text{-}[xant(P^iPr_2)_2]\}$ (**3**;

aryl = 3,5-$Me_2C_6H_3$ (**a**), C_6H_5 (**b**), 3,5-$Cl_2C_6H_5$ (**c**), 3-FC_6H_3 (**d**)) are scarcely stable, in dichloromethane or benzene, under argon. At 50 ºC, in benzene, complex **3b** quantitatively decomposes after 22 h, to give diphosphine dioxide, phenol, biphenyl, and other unidentified products. Under one oxygen atmosphere, the decomposition is faster, being completed in about 5 h.

Reactions with Carbon Monoxide

Complexes **1** also add carbon monoxide. Stirring of the red pentane solutions of these compounds, under 1 atm of the gas, for a few minutes or seconds initially affords yellow solutions from which yellow solids were isolated. They are consistent with the formula Rh(aryl)(CO){xant(P^iPr_2)$_2$} (**4**), according to the C,H elemental analysis and their electrospray HRM spectra. For the solid resulting from the **1d** precursor, suitable crystals for X-ray diffraction analysis were obtained. Figure 2 shows a view of the molecule of the new compound **4d**. Without doubt, a feature to be mentioned of the structure is the unusual *trans*-κ^2-P,P coordination of the diphosphine, which is strongly supported by the long separation between its oxygen atom and the rhodium center of 2.683 Å and the angle P(1)-Rh-P(1A) of 149.37(10)º. Thus, the geometry around the rhodium atom is almost square planar, with the phenyl ligand disposed *trans* to the carbonyl group (C(1)-Rh-C(7) = 161.2(5)º). The coordination *trans*-κ^2-P,P is unprecedented for the xant(P^iPr_2)$_2$ ligand, in the rhodium chemistry. Previously, it has been observed in the palladium complexes *trans*-Pd(Ph)(X){κ^2-P,P-[xant(P^iPr_2)$_2$]} (R = Br, CF_3)[30] and in the nickel-napthyl compounds *trans*-Ni(Np)(X){κ^2-P,P-[xant(P^iPr_2)$_2$]} (X = F, CF_3).[31]

[Insert Figure 2 here]

The ^{31}P{^{1}H}, ^{1}H, ^{13}C{^{1}H} NMR, and IR spectra of the yellow solids are consistent with the structure shown in Figure 2 and strongly support the formation of complexes Rh(aryl)(CO){κ^2-P,P-[xant(P^{i}Pr$_2$)$_2$]} (**4**; aryl = 3,5-$Me_2C_6H_3$ (**a**), C_6H_5 (**b**), 3,5-$Cl_2C_6H_3$ (**c**), 3-FC_6H_3 (**d**)), according to Scheme 5. In agreement with the equivalence of the P^{i}Pr$_2$ groups the ^{31}P{^{1}H} NMR spectra show a doublet between 39 and 41 ppm with a P-Rh coupling constant in the range 158-167 Hz, which as previously mentioned is characteristic for Rh(I) species. In accordance with the mutually *trans* disposition of the P^{i}Pr$_2$ groups, the ^{1}H NMR spectra contain the doublets of virtual triplets expected for the methyl groups of the isopropyl substituents, in the region 1.50 - 0.20 ppm. In the ^{13}C{^{1}H} NMR spectra, the CO-resonance appears as a doublet ($^1J_{C\text{-}Rh}$ ~ 58 Hz) of triplets ($^2J_{C\text{-}P}$ ~ 14 Hz) at about 201 ppm, whereas the signal corresponding to metalated carbon atom of the aryl ligand is observed between 172 and 161 ppm, also as a doublet of triplets but with C-Rh and C-P coupling constants between 24 and 28 Hz and about 14 Hz, respectively. The IR spectra display a strong ν(CO) band between 1960 and 1910 cm^{-1}.

[Insert Scheme 5 here]

Complexes **4** were obtained in high yield (70-83%) as pure yellow solids.[32] The substitution of the oxygen atom of the diphosphine by carbon monoxide should take place through the five-coordinate intermediates **A** (Scheme 5), resulting from the coordination of a carbonyl ligand to the metal center of the precursors **1**. The flexibility of the xanthene linker facilitates the replacement.

Complexes **4** rapidly evolve to the monocarbonyl-benzoyl species Rh{C(O)aryl}(CO){κ^2-P,P-[xant(P^{i}Pr$_2$)$_2$]} (**5**; aryl = 3,5-$Me_2C_6H_3$ (**a**), C_6H_5 (**b**), 3,5-$Cl_2C_6H_5$ (**c**), 3-FC_6H_3 (**d**)), when carbon monoxide is bubbled through their toluene solutions (Scheme 5). The ^{31}P{^{1}H}, ^{1}H, ^{13}C{^{1}H}

NMR, and IR spectra of these compounds support a square-planar arrangement of ligands around the metal center, which resembles that of complexes **4,** with the benzoyl group at the position of the aryl ligand. In agreement with complexes **4**, the $^{31}P\{^1H\}$ NMR spectra contain a doublet (J_{P-Rh} = 170-180 Hz) at about 43 ppm, whereas four doublets of virtual triplets due to the methyl groups of the isopropyl substituents of the diphosphine are observed in the ^1H NMR spectra, between 1.50 and 0.50 ppm. In the $^{13}C\{^1H\}$ NMR spectra, the benzoyl ligand generates two characteristic signals: one of them due to the carbonyl group, which appears at about 258 ppm, and the other one corresponding to the OC*C*-carbon atom, which is observed in the region of 150 ppm, shifted by about 20 ppm towards higher field with regard to the RhC-signal of the respective counterparts **4**. The chemical shift of the carbonyl resonance (~202 ppm) is very similar to that observed for the precursors. As expected, the IR spectra contains two ν(CO) bands; that due to carbonyl ligand appears in the range 1950-1930 cm^{-1}, whereas the band corresponding to the benzoyl group is observed in the region of 1700 cm^{-1}.

The carbonylation of complexes **4** to give the derivatives **5** is reversible. Under vacuum, complexes **5** regenerate compounds **4**. This along with the low basicity of the metal center of the $Rh(I)\{xant(P^iPr_2)_2\}$species[25a,b;33] suggests that the transformation implies the migratory insertion of the carbonyl ligand into the Rh-aryl bond and the subsequent coordination of a second carbon monoxide molecule[33] (Scheme 5). Because of the mutually *trans* disposition of the aryl ligand and the carbonyl group in complexes **4**, the regeneration of intermediates **A** by re-coordination of the oxygen atom of the diphosphine is necessary for the migratory insertion to take place. The aryl migration should afford square-planar benzoyl intermediates **B**, related to complexes **1**, bearing coordinated the oxygen atom of the diphosphine. Like complexes **1**, these intermediates could undergo the substitution of the oxygen atom of the xanthene linker by the new carbonyl ligand, to give complexes **5**, through the five-coordinate species **C**.

A few examples of rhodium(I)-benzoyl derivatives stabilized by P,N,P-pincer ligands have been reported.[8g,i] They were also formed by CO insertion into a Rh(I)-Ph bond. However, there are significant differences with regard to the carbonylation shown in Scheme 5, which seems to be related to the differences in flexibility of the linkers between the PR_2 groups of the P,O,P and P,N,P diphosphines. Thus, in contrast to xant(P^iPr_2)$_2$, the rigidity of the P,N,P diphosphines prevents square-planar species similar to complexes **4** and **5**, bearing an additional carbonyl ligand, although the formation of the benzoyl moiety also appears to take place through five-coordinate intermediates similar to **A**. Shimon, Milstein and co-workers have reported the formation of a (P,N,P)Rh{C(O)Ph} derivative, by irradiation of a benzene solution of a P,N,P-dearomatized monocarbonyl precursor. The cooperation of the dearomatized pincer appears to be necessary to promote the C-H bond activation of benzene, which affords a five-coordinate monocarbonyl-aryl key intermediate[8g]; i. e., a P,N,P-counterpart of the intermediates **A** shown in Scheme 5. Huang and co-workers have recently replaced the CH_2 arms of the classical P,N,P-pincers by NH units to prepare a benzoyl derivative related to that of the group of Shimon and Milstein, by means of the introduction of carbon monoxide into a benzene solution of the phenyl precursor. Intermediates have not been proposed in this case.[8i]

Reactions with Dimethyl Acetylenedicarboxylate

The aryl complexes **1** also react with this activated alkyne. The addition of 1.0 equiv of dimethyl acetylenedicarboxylate to toluene solutions of **1b** and **1d** initially leads to the π-alkyne complexes Rh(aryl){η^2-C(CO_2Me)≡C(CO_2Me)}{κ^3-P,O,P-xant(P^iPr_2)$_2$} (**6**; C_6H_5 (**b**), 3-FC_6H_3

(**d**)). At -20 ºC, the 3-FC_6H_3-derivative **6d** precipitated from the toluene solutions to afford an orange solid. Its IR spectrum shows a ν(C≡C) band at 1759 cm^{-1}, which strongly supports the coordination of the alkyne to the rhodium center.[35] However, the $^{31}P\{^1H\}$ NMR spectra of these compounds do not clarify the multiplicity of the coordinated C-C bond. At room temperature, the spectra contain a doublet at 26.7 ppm for **6b** and at 31.8 ppm for **6d**; the values of the P-Rh coupling constants of 145 and 133 Hz, respectively, lie in the undefined region between rhodium(I) and rhodium(III). In the ^1H NMR spectra, the most noticeable feature is the presence of four doublets of virtual triplets between 1.50 and 0.5 ppm, which are consistent with the *trans* disposition of the equivalent P^iPr_2 groups of the diphosphine. Complexes **6** are unstable and rapidly evolve to the alkenyl derivatives Rh{(*E)*-C(CO_2Me)=C(CO_2Me)Aryl}{κ^3-P,O,P-xant(P^iPr_2)$_2$} (**7**; C_6H_5 (**b**), 3-FC_6H_4 (**d**)), as a result of the *syn*-insertion of the C-C triple bond of the alkyne into the rhodium-aryl bond (Scheme 6).

[Insert Scheme 6 here]

Complexes **7** were isolated as orange solids in high yields (70% (**b**) and 75% (**d**)). Their formation was confirmed by means of the structure of X-ray diffraction analysis of **7b**. Figure 3 shows a view of the molecule. In contrast to complexes **2** and **4**, the diphosphine coordinates *mer*-κ^3-P,O,P with P(1)-Rh-P(2), P(1)-Rh-O(5), and P(2)-Rh-O(5) angles of 159.33(4)º, 81.57(7)º, and 81.89(7)º, respectively. Thus, the coordination around the metal center can be described as square-planar with the alkenyl ligand disposed *trans* to the oxygen atom of the diphosphine (C(1)-Rh-O(5) = 177.64(12)º). The C-donor ligand displays *E*-stereochemistry, with Rh-C(1) and C(1)-C(2) bond lengths of 1.976(4) and 1.372(5) Å, respectively, which compare well with those reported for other rhodium-alkenyl complexes.[26,36] The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of **7b** and **7d** are consistent with the structure shown in Figure 3. As expected for equivalent P^{i}Pr$_2$ groups, the ^{31}P{^{1}H} NMR spectra show at about 37 ppm a doublet with a P-Rh coupling constant of about 166 Hz, which agrees with the +1 oxidation state of the metal center. In the ^{13}C{^{1}H} NMR spectra, the RhC$_\alpha$-resonance of the alkenyl ligand appears as a doublet ($^1J_{C\text{-}Rh}$ ~ 42 Hz) of triplets ($^2J_{C\text{-}P}$ ~ 24 Hz) at 179.0 ppm for **7b** and at 182.4 ppm for **7d**, whereas the alkenyl-C$_\beta$ atom gives rise to a singlet at about 128 ppm.

[Insert Figure 3 here]

It should be also mentioned that the alkenyl ligand of complexes **7** is stable in benzene solution, at 70 ºC, under argon. After one week, under these conditions, the complexes were recovered unchanged. The alkenyl ligand does not undergo *E-Z* isomerization nor C-H bond activation on any substituent, in contrast to that observed for the previously reported Rh(alkenyl){κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} complexes.[26]

Conclusion

This study has revealed that the metal center of the square-planar complexes Rh(aryl){κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} coordinates molecular oxygen, carbon monoxide, and dimethyl acetylenedicarboxylate to subsequently promote transformations, involving these small molecules and ligands of the original metal coordination sphere; mainly the aryl group but also xant(P^{i}Pr$_2$)$_2$, which is oxidized in the case of dioxygen. The diphosphine plays the main role in these processes. As a consequence of the flexibility of the xanthene linker between the P^{i}Pr$_2$ groups, the diphosphine has the ability of adapting its coordination mode to the stability requirements of the reaction products; *cis*-κ^2-P,P in the dinuclear peroxide complexes **2,** *trans*-κ^2-P,P in the carbonyl derivatives **4** or *mer*-κ^3-P,O,P in the alkenyl compounds **7**; in addition to favor intermediates key for the development of particular reaction pathways. As a proof of concept of the latter, Scheme 5 shows that the coordination of the diphosphine oxygen atom provides *mer* κ^3-P,O,P intermediates **A**, which are the key for the insertion of the CO group into the Rh-aryl bond. In addition, Scheme 4 exposes that the *fac*-κ^3-P,O,P coordination of the diphosphine stabilizes the dioxygen adducts **3**, which are intermediates in the diphosphine oxidation and the formation of phenol and biphenyl. This provides a marked personality to the chemistry of the Rh{xant(P^iPr_2)$_2$} unit, which differentiates it from that of the Rh(P,N,P) systems. For instance, the dinuclear peroxide complexes **2**, the mononuclear dioxygen derivatives **3**, or the square-planar mono carbonyl compounds **4** and **5** have not precedent in the chemistry of the Rh(P,N,P) pincer-complexes and, more relevant, due to geometric constraints their preparation appears to be not possible.

Experimental

General

All reactions were carried out with exclusion of air using Schlenk-tube techniques or in a drybox. Instrumental methods and X-ray details are given in the Supplementary Data file. In the NMR spectra the chemical shifts (in ppm) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}), or external 85% H_3PO_4 (^{31}P{^{1}H}). Coupling constants *J* and *N* are given in hertz. Rh(aryl){κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (**1**; aryl = 3,5-$Me_2C_6H_3$ (**a**), C_6H_5 (**b**), 3,5-$Cl_2C_6H_3$ (**c**), 3-FC_6H_4 (**d**)) were prepared by the published methods.[9c]

Reaction of Rh(3,5-$Me_2C_6H_3$){κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (1a) with Oxygen

Complex **1a** (100 mg, 0.15 mmol) was dissolved in pentane (5 mL) and the resulting mixture was stirred during 10 min at room temperature under an oxygen atmosphere, during which time the formation of a yellow precipitate was observed. The yellow solid (**2a**) thus formed was washed with pentane (3 x 1 mL) and dried in vacuo. Yield: 92 mg (88%). Anal. calcd. for $C_{70}H_{98}O_6P_4Rh_2$: C, 61.58; H, 7.23. Found: C, 61.23; H, 7.18. IR (ATR, cm^{-1}): ν(O-O) 875 (m). Spectroscopic data for **3a**: HRMS (electrospray, *m/z*): calcd. for $C_{37}H_{53}NO_3P_2Rh$ $[M + CH_3CN + H]^+$, 724.2550; found, 724.2518. ^1H NMR (300.13 MHz, CD_2Cl_2, 298 K): δ 7.52 (d, J_{H-H} = 7.6, 2H, CH-arom POP), 7.44 (dd, J_{H-H} = 7.6, J_{H-P} = 7.0, 2H, CH-arom POP), 7.23 (t, J_{H-H} = 7.6, 2H, CH-arom POP), 6.84 (s, 2H, *o*-CH 3,5-$Me_2C_6H_3$), 6.38 (s, 1H, *p*-CH 3,5-$Me_2C_6H_3$), 2.79 (m, 2H, $PCH(CH_3)_2$), 2.53 (m, 2H, $PCH(CH_3)_2$), 2.08 (s, 6H, CH_3 Ph), 1.85 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.22 (dd, $^3J_{H-H}$ = 7.0, $^3J_{H-P}$ = 16.6, 6H, $PCH(CH_3)_2$), 1.19 (dd, $^3J_{H-H}$ = 6.8, $^3J_{H-P}$ = 13.7, 6H, $PCH(CH_3)_2$), 0.93 (dd, $^3J_{H-H}$ = 7.0, $^3J_{H-P}$ = 14.6, 6H, $PCH(CH_3)_2$), 0.88 (dd, $^3J_{H-H}$ = 6.9, $^3J_{H-P}$ = 16.5, 6H, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.48 MHz, CD_2Cl_2, 298 K): δ 38.9 (d, $^1J_{P-Rh}$ = 155.3). Its low stability, as well as its low solubility, in CD_2Cl_2 prevented its characterization by $^{13}C\{^1H\}$ NMR spectroscopy. IR (CCl_4, cm^{-1}): ν(O-O) 1064 (m).

Reaction of $Rh(C_6H_5)\{\kappa^3\text{-P,O,P-}[xant(P^iPr_2)_2]\}$ (1b) with Oxygen

Complex **1b** (100 mg, 0.16 mmol) was dissolved in pentane (5 mL) and the resulting mixture was stirred during 30 min at room temperature under an oxygen atmosphere, during which time the formation of a yellow precipitate was observed. The yellow solid (**2b**) thus formed was washed with pentane (3 x 1 mL) and dried in vacuo. Yield: 96 mg (91%). Anal. calcd. for $C_{66}H_{90}O_6P_4Rh_2$: C, 60.55; H, 6.93. Found: C, 60.58; H, 6.95. IR (cm^{-1}): ν(O-O) 873 (m). Spectroscopic data for **3b**: HRMS (electrospray, *m/z*): calcd. for $C_{33}H_{45}O_3P_2Rh$ $[M]^+$, 655.1972; found, 655.2017. ^1H NMR (300.13 MHz, CD_2Cl_2, 298 K): δ 7.52 (d, J_{H-H} = 7.0, 2H, CH-arom POP), 7.48 (t, J_{H-H} = 7.0, 2H, CH-arom POP), 7.35-7.25 (m, 4H, CH-arom POP and C_6H_5), 6.83-6.74 (m, 3H, C_6H_5), 2.82 (m, 2H, $PCH(CH_3)_2$), 2.51 (m, 2H, $PCH(CH_3)_2$), 1.85 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.28 (dd, $^3J_{H\text{-}H}$ = 6.9, $^3J_{H\text{-}P}$ = 13.2, 6H, $PCH(CH_3)_2$), 1.20 (dd, $^3J_{H\text{-}H}$ = 6.8, $^3J_{H\text{-}P}$ = 16.5, 6H, $PCH(CH_3)_2$), 0.92 (dd, $^3J_{H\text{-}H}$ = 7.1, $^3J_{H\text{-}P}$ = 16.6, 6H, $PCH(CH_3)_2$), 0.81 (dd, $^3J_{H\text{-}H}$ = 6.9, $^3J_{H\text{-}P}$ = 16.6, 6H, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 298 K): δ 39.4 (d, $^1J_{P\text{-}Rh}$ = 154.3). Its low stability, as well as its low solubility, in CD_2Cl_2 prevented its characterization by $^{13}C\{^1H\}$ NMR spectroscopy. IR (CCl_4, cm^{-1}): ν(O-O) 1064 (m).

Reaction of $Rh(3,5\text{-}Cl_2C_6H_3)\{\kappa^3\text{-}P,O,P\text{-}[xant(P^iPr_2)_2]\}$ (1c) with Oxygen

Complex **1c** (100 mg, 0.14 mmol) was dissolved in pentane (5 mL) and the resulting mixture was stirred during 5 min at room temperature under an oxygen atmosphere, during which time the formation of a yellow precipitate was observed. The yellow solid (**2c**) thus formed was washed with pentane (3 x 1 mL) and dried in vacuo. Yield: 91 mg (87%). Anal. Calcd. for $C_{66}H_{86}Cl_4O_6P_4Rh_2$: C, 54.79; H, 5.99. Found: C, 54.63; H, 5.85. IR (ATR, cm^{-1}): ν(O-O) 874 (m). Spectroscopic data for **3c**: HRMS (electrospray, *m*/*z*): calcd. for $C_{35}H_{47}Cl_2NO_3P_2Rh$ [M + CH_3CN + H]$^+$ 764.1458; found 764.1430. ^1H NMR (300.08 MHz, CD_2Cl_2, 298 K): δ 7.54 (d, $J_{H\text{-}H}$ = 7.6, 2H, CH-arom POP), 7.49 (m, 2H, CH-arom POP), 7.31 (t, $J_{H\text{-}H}$ = 7.6, 2H, CH-arom POP), 7.22 (s, 2H, *o*-CH $3,5\text{-}Cl_2C_6H_3$), 6.84 (s, $J_{H\text{-}H}$ = 1.6, 1H, *p*-CH $3,5\text{-}Cl_2C_6H_3$), 2.85 (m, 2H, $PCH(CH_3)_2$), 2.48 (m, 2H, $PCH(CH_3)_2$), 1.85 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.30 (dd, $^3J_{H\text{-}H}$ = 6.7, $^3J_{H\text{-}P}$ = 13.8, 6H, $PCH(CH_3)_2$), 1.20 (dd, $^3J_{H\text{-}H}$ = 6.9, $^3J_{H\text{-}P}$ = 17.0, 6H, $PCH(CH_3)_2$), 0.92 (dd, $^3J_{H\text{-}H}$ = 7.1, $^3J_{H\text{-}P}$ = 14.6, 6H, $PCH(CH_3)_2$), 0.85 (dd, $^3J_{H\text{-}H}$ = 6.4, $^3J_{H\text{-}P}$ = 17.4, 6H, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.48 MHz, CD_2Cl_2, 298 K): δ 40.1 (d, $^1J_{P\text{-}Rh}$ = 147.6). Its low stability, as well as its low solubility, in CD_2Cl_2 prevented its characterization by $^{13}C\{^1H\}$ NMR spectroscopy. IR (CCl_4, cm^{-1}): ν(O-O) 1064 (m).

Reaction of $Rh(3\text{-}FC_6H_4)\{\kappa^3\text{-}P,O,P\text{-}[xant(P^iPr_2)_2]\}$ (1d) with Oxygen

Complex **1d** (100 mg, 0.16 mmol) was dissolved in pentane (5 mL) and the resulting mixture was stirred during 10 min at room temperature under an oxygen atmosphere, during which time the formation of a yellow precipitate was observed. The yellow solid (**2d**) thus formed was washed with pentane (3 x 1 mL) and dried in vacuo. Yield: 97.4 mg (93%). Anal. Calcd. for $C_{66}H_{88}F_2O_6P_4Rh_2$: C, 58.93; H, 6.59. Found: C, 58.69; H, 6.62. IR (cm^{-1}): ν(O-O) 875 (m). Spectroscopic data for **3d**: HRMS (electrospray, *m*/*z*): calcd. for $C_{33}H_{45}FO_3P_2Rh$ $[M + H]^+$, 673.1878; found, 673.1866. ^1H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 7.53 (dd, $J_{H\text{-}H}$ = 7.5, $J_{H\text{-}H}$ = 1.3, 2H, CH-arom POP), 7.48 (ddd, $J_{H\text{-}H}$ = 7.5, $J_{H\text{-}P}$ = 5.7, $J_{H\text{-}H}$ = 1.3, 2H, CH-arom POP), 7.30 (dt, $J_{H\text{-}H}$ = 7.5, $J_{H\text{-}P}$ = 1.3, 2H, CH-arom POP), 7.12 (d, $J_{H\text{-}H}$ = 8.5, 1H, *o*-CH 3-FC_6H_4), 7.09 (br d, $J_{H\text{-}F}$ = 10.0, 1H, *o*-CH 3-FC_6H_4), 6.71 (dt, $J_{H\text{-}H}$ = 7.0, $J_{H\text{-}F}$ = 7.0, 1H, *m*-CH 3-FC_6H_4), 6.50 (ddd, $J_{H\text{-}H}$ = 8.1, $J_{H\text{-}F}$ = 8.1, $J_{H\text{-}H}$ = 2.3, 1H, *p*-CH 3-FC_6H_4), 2.84 (m, 2H, $PCH(CH_3)_2$), 2.49 (m, 2H, $PCH(CH_3)_2$), 1.85 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.31 (dd, $^3J_{H\text{-}H}$ = 7.4, $^3J_{H\text{-}P}$ = 13.7, 6H, $PCH(CH_3)_2$), 1.20 (dd, $^3J_{H\text{-}H}$ = 7.0, $^3J_{H\text{-}P}$ = 16.8, 6H, $PCH(CH_3)_2$), 0.92 (dd, $^3J_{H\text{-}H}$ = 7.0, $^3J_{H\text{-}P}$ = 14.2, 6H, $PCH(CH_3)_2$), 0.81 (dd, $^3J_{H\text{-}H}$ = 6.9, $^3J_{H\text{-}P}$ = 16.8, 6H, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.48 MHz, CD_2Cl_2, 298 K): δ 40.0 (d, $^1J_{P\text{-}Rh}$ = 152.5). Its low stability, as well as its low solubility, in CD_2Cl_2 prevented its characterization by $^{13}C\{^1H\}$ NMR spectroscopy. IR (CCl_4, cm^{-1}): ν(O-O) 1064 (m).

Reaction of Rh(3,5-$Me_2C_6H_3$){κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (1a) with CO: Formation of Rh(3,5-$Me_2C_6H_3$)(CO){κ^2-P,P-[xant(P^iPr_2)$_2$]} (4a) and Rh{C(O)C_6H_5}(CO){κ^2-P,P-[xant(P^iPr_2)$_2$]} (5b)

A solution of complex **1a** (50 mg, 0.07 mmol) in pentane (5 mL) was exposed to a CO atmosphere. The color of the solution immediately changes to yellow. Its evaporation to dryness yielded a yellow solid. The $^{31}P\{^1H\}$ NMR spectrum shows a mixture of **4a** and **5a** in a molar ratio of 65:35. Bubbling CO through toluene solutions of the solid affords **5a**. Under vacuum, the mixture of **4a** and **5a** is regenerated.

Spectroscopic data for **4a**: ^{1}H NMR (400.13 MHz, toluene-d_8, 298 K): δ 7.23 (d, $J_{\text{H-H}}$ = 7.3, $J_{\text{H-H}}$ = 1.9, 2H, CH-arom POP), 7.12 (m, 2H, CH-arom POP), 7.0-6.9 (m, 4H, 2CH POP + 2 *o*-CH 3,5-$Me_2C_6H_3$), 6.56 (s, *p*-CH 3,5-$Me_2C_6H_3$), 2.23 (m, 4H, $PCH(CH_3)_2$), 1.59 (s, 6H, 3,5-$Me_2C_6H_3$), 1.33 (dvt, $^{3}J_{\text{H-H}}$ = 8.1, *N* = 17.0, 6H, $PCH(CH_3)_2$), 1.31 (s, 3H, CH_3), 1.23 (dvt, $^{3}J_{\text{H-H}}$ = 7.0, *N* = 16.7, 6H, $PCH(CH_3)_2$), 1.18 (s, 3H, CH_3), 0.92 (dvt, $^{3}J_{\text{H-H}}$ = 6.3, *N* = 12.4, 6H, $PCH(CH_3)_2$), 0.29 (dvt, $^{3}J_{\text{H-H}}$ = 7.0, *N* = 13.9, 6H, $PCH(CH_3)_2$). ^{13}C{^{1}H}-apt NMR (100.63 MHz, toluene-d_8, 263 K): δ 201.5 (dt, $^{1}J_{\text{C-Rh}}$ = 58.2, $^{2}J_{\text{C-P}}$ = 14.5, Rh-CO), 161.8 (dt, $^{1}J_{\text{C-Rh}}$ = 24.1, $^{2}J_{\text{C-P}}$ = 13.5, Rh-C), 155.3 (vt, *N* = 9.1, C-arom POP), 138.7 (s, CH Ph), 133.7 (vt, *N* = 4.0, C-arom POP), 133.3 (s, C Ph), 131.2, 125.9, 123.6 (all s, CH-arom POP), 121.2 (s, CH Ph), 119.5 (vt, *N* = 30.4, C-arom POP), 35.5 (s, $C(CH_3)_2$), 33.1 (s, $C(CH_3)_2$), 31.4 (vt, *N* = 24.0, $PCH(CH_3)_2$), 25.0 (vt, *N* = 19.1, $PCH(CH_3)_2$), 23.1 (s, $C(CH_3)_2$), 19.4 (vt, *N* = 15.9, $PCH(CH_3)_2$), 19.2 (s, $PCH(CH_3)_2$), 18.1 (s, CH_3), 17.4 (s, $PCH(CH_3)_2$). ^{31}P{^{1}H} NMR (161.98 MHz, toluene-d_8, 298 K): δ 39.2 (d, $^{1}J_{\text{P-Rh}}$ = 166.8). IR (pentane, cm^{-1}): ν(CO) 1937 (s).

Spectroscopic data for **5a**: ^{1}H NMR (400.13 MHz, toluene-d_8, 273 K): δ 8.29 (br, 2H, 3,5-$Me_2C_6H_3$), 7.30 (d, $J_{\text{H-H}}$ = 7.7, 2H, CH-arom POP), 6.98 (t, $^{3}J_{\text{H-H}}$ = 7.3, 2H, CH-arom POP), 6.84 (m, 2H, CH-arom POP), 6.74 (s, 1H, 3,5-$Me_2C_6H_3$), 2.24 (m, 4H, $PCH(CH_3)_2$), 2.19 (s, 6H, 3,5-$Me_2C_6H_3$), 1.30-1.23 (m, 18H, 2 CH_3 POP + 2 $PCH(CH_3)_2$), 0.88, 0.48 (m, each 6H, $PCH(CH_3)_2$). ^{13}C{^{1}H}-apt NMR (100.63 MHz, toluene-d_8, 273 K): δ 258.7 (br, RhC(O)Ph), 202.8 (dt, $^{1}J_{\text{C-Rh}}$ = 57.3, $^{2}J_{\text{C-P}}$ = 14.6, Rh-CO), 157.3 (vt, *N* = 8.5, C-arom POP), 150.9 (t, $^{3}J_{\text{C-P}}$ = 6.8, C 3,5-$Me_2C_6H_3$), 137.0 (s, C 3,5-$Me_2C_6H_3$), 134.1 (vt, *N* = 5.4, C-arom POP), 131.2 (s, CH 3,5-$Me_2C_6H_3$), 131.0 (s, CH-arom POP), 129.6 (s, CH 3,5-$Me_2C_6H_3$), 126.7, 123.5 (both s, CH-arom POP), 116.5 (vt, *N* = 33.1, C-arom POP), 36.1 (s, *C*(CH$_3$)$_2$), 33.4, 26.9 (both s, C(*C*H$_3$)$_2$), 31.2, 29.9 (both br, P*C*H(CH$_3$)$_2$), 21.8 (s, CH$_3$ Ph), 19.7 (m, PCH(*C*H$_3$)$_2$), 19.2, 18.8 (both s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (161.98 MHz, toluene-d_8, 298 K): δ 42.4 (d, $^1J_{\text{P-Rh}}$ = 179.9). IR (pentane, cm^{-1}): ν(CO) 1937 (s), ν(C=O) 1723 (w).

Reaction of Rh(C$_6$H$_5$){κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (1b) with CO: Formation of Rh(C$_6$H$_5$)(CO){κ^2-P,P-[xant(P^{i}Pr$_2$)$_2$]} (4b)

A solution of complex **1b** (50 mg, 0.07 mmol) in pentane (5 mL) was exposed to a CO atmosphere, changing the color of the solution to yellow. Immediately it was evaporated to dryness to afford a yellow solid. Yield: 36 mg (70%). Anal. Calcd. for C$_{34}$H$_{45}$O$_2$P$_2$Rh: C, 62.77; H, 6.97. Found: C, 62.33; H, 7.20. ^{1}H NMR (300.13 MHz, toluene-d_8, 298 K): δ 7.22 (dd, $J_{\text{H-H}}$ = 7.3, $J_{\text{H-H}}$ = 1.9, 2H, CH-arom POP), 7.10 (br, 2H, Ph), 6.95 (t, $^3J_{\text{H-H}}$ = 7.4, 2H, CH-arom POP), 6.91 (m, 2H, CH-arom POP), 6.56 (br, 3H, Ph), 2.22 (m, 4H, PC*H*(CH$_3$)$_2$), 1.59 (s, 3H, CH$_3$), 1.33 (dvt, $^3J_{\text{H-H}}$ = 9.5, *N* = 19.4, 6H, PCH(C*H*$_3$)$_2$), 1.32 (dvt, $^3J_{\text{H-H}}$ = 8.0, *N* = 17.6, 6H, PCH(C*H*$_3$)$_2$), 1.18 (s, 3H, CH$_3$), 0.90 (dvt, $^3J_{\text{H-H}}$ = 6.6, *N* = 12.8, 6H, PCH(C*H*$_3$)$_2$), 0.28 (dvt, $^3J_{\text{H-H}}$ = 7.0, *N* = 13.9, 6H, PCH(C*H*$_3$)$_2$). ^{13}C{^{1}H}-apt NMR (100.63 MHz, toluene-d_8, 273 K): δ 201.6 (dt, $^1J_{\text{C-Rh}}$ = 58.6, $^2J_{\text{C-P}}$ = 14.0, Rh-CO), 161.8 (dt, $^1J_{\text{C-Rh}}$ = 25.2, $^2J_{\text{C-P}}$ = 14.3, Rh-C), 155.3 (vt, *N* = 9.2, *C*-arom), 138.8 (s, CH Ph), 133.3 (vt, *N* = 3.5, *C*-arom), 131.2 (s, *C*H-arom), 126.0 (s, *C*H-arom), 125.9 (s, CH Ph), 123.6 (s, CH arom), 121.2 (s, CH Ph), 119.65 (vt, *N* = 30.0, *C*-arom), 35.5 (s, *C*(CH$_3$)$_2$), 33.2 (s, C(*C*H$_3$)$_2$), 31.5 (vt, *N* = 24.1, P*C*H(CH$_3$)$_2$), 25.1 (vt, *N* = 18.0, P*C*H(CH$_3$)$_2$), 23.2 (s, C(*C*H$_3$)$_2$), 19.4 (vt, *N* = 16.9, PCH(*C*H$_3$)$_2$), 19.2, 18.1, 17.5 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.50 MHz, toluene-d_8, 298 K): δ 39.7 (d, $^1J_{\text{P-Rh}}$ = 166.5). IR (pentane, cm^{-1}): ν(CO) 1938 (s).

Reaction of Rh(3,5-$Cl_2C_6H_3$){κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (1c) with CO: Formation of Rh(3,5-$Cl_2C_6H_3$)(CO){κ^2-P,P-[xant(P^iPr_2)$_2$]} (4c)

A solution of complex **1c** (50 mg, 0.07 mmol) in pentane (5 mL) was stirred under a CO atmosphere during 1 min at room temperature, changing the color from red to yellow. After this time, it was evaporated to dryness to afford a yellow solid. Yield: 43 mg (83%). Anal. Calcd. for $C_{34}H_{43}Cl_2O_2P_2Rh$: C, 56.76; H, 6.02. Found: C, 56.43; H, 6.23. HRMS (electrospray, *m*/*z*) calcd. for $C_{33}H_{44}Cl_2OP_2Rh$ [M-CO+H]$^+$: 691.1294; found: 691.1292. ^{1}H NMR (300.13 MHz, toluene-d_8, 298 K): δ 7.24 (d, $^3J_{H-H}$ = 7.6, 2H, CH-arom POP), 6.92 (t, $^3J_{H-H}$ = 7.7, 2H, CH-arom POP), 6.81 (m, 2H, CH-arom POP), 6.70 (br, 1H, 3,5-$Cl_2C_6H_3$), 2.18 (m, 4H, PC*H*(CH_3)$_2$), 1.64 (s, 3H, CH_3), 1.23 (dvt, $^3J_{H-H}$ = 8.0, *N* = 14.4, 6H, PCH(C*H*$_3$)$_2$), 1.20 (dvt, $^3J_{H-H}$ = 8.7, *N* = 16.2, 6H, PCH(C*H*$_3$)$_2$), 1.19 (s, 3H, CH_3), 0.83 (dvt, $^3J_{H-H}$ = 6.5, *N* = 12.1, 6H, PCH(C*H*$_3$)$_2$), 0.30 (dvt, $^3J_{H-H}$ = 7.2, *N* = 13.9, 6H, PCH(C*H*$_3$)$_2$). ^{1}H NMR (300.13 MHz, toluene-d_8, 213 K, 3,5-$Cl_2C_6H_3$ group protons): δ 8.57 (s, 1H), 6.79 (s, 1H), 5.48 (s, 1H). ^{13}C{^{1}H}-apt NMR (75.48 MHz, toluene-d_8, 273 K): δ 200.7 (dt, $^1J_{C-Rh}$ = 59.2, $^2J_{C-P}$ = 13.9, Rh-CO), 172.1 (dt, $^1J_{C-Rh}$ = 28.4, $^2J_{C-P}$ = 15.2, Rh-C), 155.2 (vt, *N* = 8.4, C-arom POP), 137.0, 135.7 (both br s, *o*-CH 3,5-$Cl_2C_6H_3$), 133.5 (s, C-arom POP), 131.5 (s, *p*-CH 3,5-$Cl_2C_6H_3$), 130.1 (br s, C 3,5-$Cl_2C_6H_3$), 126.9, 124.4, 120.8 (all s, CH-arom POP), 118.1 (vt, *N* = 31.6, C-arom POP), 35.8 (s, *C*(CH_3)$_2$), 33.4 (s, C(*C*H$_3$)$_2$), 30.8 (vt, *N* = 22.3, P*C*H(CH_3)$_2$), 25.0 (vt, *N* = 18.0, P*C*H(CH_3)$_2$), 24.1 (s, C(*C*H$_3$)$_2$), 19.4, 18.6, 17.3 (all s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.50 MHz, toluene-d_8, 298 K): δ 41.2 (d, $^1J_{P-Rh}$ = 157.9). IR (pentane, cm^{-1}): ν(CO) 1952 (s).

Reaction of Rh(3-FC_6H_4){κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (1d) with CO: Formation of Rh(3-FC_6H_4) (CO){κ^2-P,P-[xant(P^iPr_2)$_2$]} (4d)

A solution of complex **1d** (50 mg, 0.08 mmol) in pentane (5 mL) was stirred under CO atmosphere during 5 min at room temperature, changing the color from red to yellow. After this time, it was evaporated to dryness to afford a yellow solid. Yield: 36 mg (70%). Anal. Calcd. for $C_{34}H_{44}FO_2P_2Rh$: C, 61.08; H, 6.63. Found: C, 60.76; H, 6.85. HRMS (electrospray, *m*/*z*): calcd. for $C_{34}H_{45}FO_2P_2Rh$ $[M + H]^+$ 657.1928; found 657.1895. ^1H NMR (300.13 MHz, toluene-d_8, 298 K): δ 7.29 (d, J_{H-H} = 7.5, 2H, CH-arom POP), 7.23 (br, 1H, 3-FC_6H_4), 7.00 (t, $^3J_{H-H}$ = 7.5, 2H, CH-arom POP), 6.94-6.90 (m, 3H, CH-arom POP + 3-FC_6H_4), 6.49 (br, 1H, 3-FC_6H_4), 6.33 (m, 1H, 3-FC_6H_4), 2.26 (m, 4H, $PCH(CH_3)_2$), 1.65 (s, 3H, CH_3), 1.37 (dvt, $^3J_{H-H}$ = 5.6, *N* = 13.5, 6H, $PCH(CH_3)_2$), 1.34 (dvt, $^3J_{H-H}$ = 7.8, *N* = 15.0, 6H, $PCH(CH_3)_2$), 1.24 (s, 3H, CH_3), 0.95 (dvt, $^3J_{H-H}$ = 6.4, *N* = 12.7, 6H, $PCH(CH_3)_2$), 0.36 (dvt, $^3J_{H-H}$ = 7.4, *N* = 14.4, 6H, $PCH(CH_3)_2$). $^{13}C\{^1H\}$-apt NMR (100.62 MHz, toluene-d_8, 273 K): δ 201.6 (dt, $^1J_{C-Rh}$ = 58.8, $^2J_{C-P}$ = 13.9, Rh-CO), 167.9 (m, Rh-C), 161.0 (br d, $^1J_{C-F}$ = 231.0, C-F), 155.5 (vt, *N* = 8.9, C-arom POP), 134.8 (br, CH 3-FC_6H_4), 133.7 (vt, *N* = 4.1, C-arom POP), 131.6 (s, CH-arom POP), 126.7 (s, CH-arom POP), 125.0 (dt, J_{C-F} = 14.4, J_{C-P} = 3.4, CH C_6H_4-3-F), 124.3 (dt, J_{C-F} = 18.3, J_{C-P} = 2.0, CH 3-FC_6H_4), 124.2 (s, CH-arom POP), 119.7 (vt, *N* = 30.4, C-arom POP), 107.9 (d, J_{C-F} = 21.4, CH 3-FC_6H_4), 35.9 (s, $C(CH_3)_2$), 33.7 (s, $C(CH_3)_2$), 30.8 (vt, *N* = 23.9, $PCH(CH_3)_2$), 25.5 (vt, *N* = 20.5, $PCH(CH_3)_2$), 24.0 (s, $C(CH_3)_2$), 19.6, 18.6, 17.8 (all s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.98 MHz, toluene-d_8, 298 K): δ 40.4 (d, $^1J_{P-Rh}$ = 163.2). IR (pentane, cm^{-1}): ν(CO) 1958 (s).

Reaction of $Rh(C_6H_5)(CO)\{\kappa^2\text{-}P,P\text{-}[xant(P^iPr_2)_2]\}$ (4b) with CO: Formation of $Rh\{C(O)C_6H_5\}(CO)\{\kappa^2\text{-}P,P\text{-}[xant(P^iPr_2)_2]\}$ (5b)

CO was bubbled through toluene or pentane solutions of **4b** for 20 sec. The CO atmosphere was then replaced by an argon atmosphere, and immediately the NMR or the IR spectra were recorded. ^1H NMR (400.13 MHz, toluene-d_8, 298K): δ 8.57 (br, 2H, CH Ph), 7.25 (d, J_{H-H} = 7.5, 2H, CH-arom POP), 7.12-6.84 (m, 6H, 2H Ph + 4H CH-arom POP), 6.56 (br, 1H, CH Ph), 2.23 (m, 4H, PC*H*(CH$_3$)$_2$), 1.33-1.19 (m, 18H, 2 CH$_3$ + PCH(C*H*$_3$)$_2$), 0.92-0.81 (m, 12H, PCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100.63 MHz, toluene-*d*$_8$, 273 K): δ 258.1 (br, Rh-*C*(O)Ph), 202.0 (dt, $J_{\text{C-Rh}}$ = 56.8, $J_{\text{C-P}}$ = 15.4, Rh-C), 156.9 (vt, *N* = 8.2, C-arom POP), 150.2 (t, $^3J_{\text{C-P}}$ = 6.6, C Ph), 138.9 (s, CH Ph), 133.7 (vt, *N* = 4.2, C-arom POP), 130.5 (s, CH-arom POP), 129.2 (s, CH Ph), 126.3 (s, CH-arom POP), 123.1 (s, CH-arom POP), 121.2 (s, CH Ph), 116.0 (vt, *N* = 34.4, C-arom POP), 35.6 (s, *C*(CH$_3$)$_2$), 33.2 (s, C(*C*H$_3$)$_2$), 31.5 (m, P*C*H(CH$_3$)$_2$), 25.1 (vt, *N* = 19.4, P*C*H(CH$_3$)$_2$), 23.3 (s, C(*C*H$_3$)$_2$), 19.4 (vt, *N* = 16.2, PCH(*C*H$_3$)$_2$), 19.2, 18.1, 17.5 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (161.98 MHz, toluene-*d*$_8$, 298 K): δ 42.8 (d, $J_{\text{P-Rh}}$ = 179.2). IR (pentane, cm^{-1}): ν(CO) 1938 (s), ν(C=O) 1723 (w).

Reaction of Rh(3,5-Cl$_2$C$_6$H$_3$)(CO){κ^2-P,P-[xant(P^{i}Pr$_2$)$_2$]} (4c) with CO: Formation of Rh{C(O)-3,5-Cl$_2$C$_6$H$_3$}(CO){κ^2-P,P-[xant(P^{i}Pr$_2$)$_2$]} (5c)

CO was bubbled through toluene or pentane solutions of **4c** for 1 min. The CO atmosphere was then replaced by an argon atmosphere, and immediately the NMR or the IR spectra were recorded. ^{1}H NMR (400.13 MHz, toluene-*d*$_8$, 273 K): δ 7.21 (d, $J_{\text{H-H}}$ = 7.6, 2H, CH-arom POP), 6.98 (s, 2H, 3,5-Cl$_2$C$_6$H$_3$), 6.94 (t, $^3J_{\text{H-H}}$ = 7.4, 2H, CH-arom POP), 6.83 (m, 2H, CH-arom POP), 6.75 (s, 1H, 3,5-Cl$_2$C$_6$H$_3$), 2.18 (m, 4H, PC*H*(CH$_3$)$_2$), 1.51 (s, 3H, CH$_3$), 1.26 (s, 3H, CH$_3$),1.20 (dvt, $^3J_{\text{H-H}}$ = 6.6, *N* = 17.8, 6H, PCH(C*H*$_3$)$_2$), 1.15 (dvt, $^3J_{\text{H-H}}$ = 6.7, *N* = 15.0, 6H, PCH(C*H*$_3$)$_2$), 0.85 (dvt, $^3J_{\text{H-H}}$ = 6.6, *N* = 13.1, 6H, PCH(C*H*$_3$)$_2$), 0.41 (dvt, $^3J_{\text{H-H}}$ = 6.5, *N* = 12.8, 6H, PCH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (161.98 MHz, C$_7$D$_8$, 298 K): δ 43.7 (d, $^1J_{\text{P-Rh}}$ = 170.2). The ^{13}C{^{1}H} NMR spectrum could not be recorded due to its low stability. IR (pentane, cm^{-1}): ν(CO) 1935 (s), ν(CO) 1717 (w).

Reaction of Rh(3-FC$_6$H$_4$)(CO){κ^2-P,P-[xant(P^{i}Pr$_2$)$_2$]} (4d) with CO: Formation of Rh{C(O)-3-FC$_6$H$_4$}(CO){κ^2-P,P-[xant(P^{i}Pr$_2$)$_2$]} (5d)

CO was bubbled through toluene or pentane solutions of **4d** for 1 min. The CO atmosphere was then replaced by an argon atmosphere, and immediately the NMR or the IR spectra were recorded. ^{1}H NMR (300.13 MHz, toluene-*d*$_8$, 298 K): δ 8.60 (br, 1H, 3-FC$_6$H$_4$), 8.09 (br, 1H, 3-FC$_6$H$_4$), 7.28 (d, J_{H-H} = 7.6, 2H, CH-arom POP), 6.96 (t, $^3J_{H-H}$ = 7.6, 2H, CH-arom POP), 6.88-6.80 (m, 3H, 2 CH-arom POP + CH 3-FC$_6$H$_4$), 6.75 (m, 1H, 3-FC$_6$H$_4$), 2.20 (m, 4H, PC*H*(CH$_3$)$_2$), 1.30-1.16 (m, 18H, 2 CH$_3$ + 2 PCH(C*H*$_3$)$_2$), 0.86 (dvt, $^3J_{H-H}$ = 6.8, *N* = 13.6, 6H, PCH(C*H*$_3$)$_2$), 0.32 (dvt, $^3J_{H-H}$ = 7.1, *N* = 14.1, 6H, PCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100.63 MHz, toluene-*d*$_8$, 253 K): δ 258.1 (m, Rh-*C*(O)-3-FC$_6$H$_4$), 201.5 (dt, $^1J_{C-Rh}$ = 56.0, $^2J_{C-P}$ = 16.0, Rh-CO), 163.3 (d, $^1J_{C-F}$ = 246.0, C-F), 156.7 (vt, *N* = 8.4, C-arom POP), 152.3 (dt, $^3J_{C-P}$ = 6.1, $^3J_{C-F}$ = 2.2, C 3-FC$_6$H$_4$), 133.6 (vt, *N* = 4.0, C-arom POP), 131.1 (s, CH 3-FC$_6$H$_4$), 130.4 (s, CH-arom POP), 129.1 (s, CH 3-FC$_6$H$_4$), 126.4 (s, CH-arom POP), 123.7 (s, CH 3-FC$_6$H$_4$), 123.1 (s, CH-arom POP), 115.7 (d, J_{C-F} = 21.7, CH 3-FC$_6$H$_4$), 115.4 (vt, *N* = 32.9, C-arom POP), 35.5 (s, *C*(CH$_3$)$_2$), 33.5 (s, C(*C*H$_3$)$_2$), 30.6 (vt, *N* = 28.1, P*C*H(CH$_3$)$_2$), 24.3 (vt, *N* = 20.9, P*C*H(CH$_3$)$_2$), 23.4 (s, C(*C*H$_3$)$_2$), 19.2 (s, PCH(*C*H$_3$)$_2$), 18.6 (vt, *N* = 12.7, PCH(*C*H$_3$)$_2$), 17.9, 17.1 (both s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (161.98 MHz, toluene-*d*$_8$, 298 K): δ 43.0 (d, $^1J_{P-Rh}$ = 174.6). IR (pentane, cm^{-1}): ν(CO) 1936 (s), ν(CO) 1723 (w).

Spectroscopic Detection of Rh(C$_6$H$_5$){η^2-C(CO$_2$Me)≡C(CO$_2$Me)}{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (6b)

A solution of **1b** (15 mg, 0.024 mmol) in toluene-*d*$_8$ (0.5 mL) was placed in an NMR tube and was treated with dimethyl acetylenedicarboxylate (3 μL, 0.024 mmol). The resulting solution was periodically checked by ^{31}P{^{1}H} and ^{1}H NMR spectroscopies. The ^{31}P{^{1}H} NMR spectrum recorded after 10 min shows a mixture of **7b** and **6b** in a ratio 3 : 97. ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.42-6.80 (m, 8H, 6 CH-arom POP, 2 CH Ph), 6.73-6.22 (m, 3H, Ph), 3.73 (s, 6H, CO_2CH_3), 3.28 (m, 2H, PC*H*(CH_3)$_2$), 2.60 (m, 2H, PC*H*(CH_3)$_2$), 1.59 (s, 3H, CH_3), 1.52 (dvt, $^3J_{H-H}$ = 7.6, *N* = 16.4, 6H, PCH(C*H*$_3$)$_2$), 1.38 (dvt, $^3J_{H-H}$ = 7.4, *N* = 16.0, 6H, PCH(C*H*$_3$)$_2$), 1.30 (s, 3H, CH_3), 1.04 (dvt, $^3J_{H-H}$ = 6.2, *N* = 12.2, 6H, PCH(C*H*$_3$)$_2$), 0.37 (br m, 6H, PCH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 298 K): δ 26.7 (d, $^1J_{Rh-P}$ = 145.1).

Spectroscopic Detection of Rh(3-FC$_6$H$_4$){η^2-C(CO$_2$Me)≡C(CO$_2$Me)}{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (6d)

A solution of **1d** (15 mg, 0.023 mmol) in toluene-*d*$_8$ (0.5 mL) placed in an NMR tube was treated with dimethyl acetylenedicarboxylate (3 μL, 0.023 mmol). The ^{1}H and ^{31}P{^{1}H} recorded after 10 min at room temperature shows a mixture of **7d** and **6d** in a ratio 7 : 93. If the resulting solution is cooled immediately at -20 ºC an orange microcrystalline solid is formed. Upon removal of the solution, complex **6d** was isolated as an orange solid. Yield: 16 mg (87 %). Anal. Calcd. for $C_{39}H_{50}FO_5P_2Rh$: C, 59.85; H, 6.44. Found: C, 59.54; H, 6.74. ^{1}H NMR (300.13 MHz, toluene-*d*$_8$, 298 K): δ 7.41-6.88 (m, 8H, 4 CH-arom POP, 4 CH Ph), 6.42 (m, 2H, CH-arom POP), 3.71 (s, 6H, CO_2CH_3), 3.00 (m, 2H, PC*H*(CH_3)$_2$), 2.47 (m, 2H, PC*H*(CH_3)$_2$), 1.66 (s, 3H, CH_3), 1.40 (dvt, $^3J_{H-H}$ = 8.2, *N* = 16.8, 6H, PCH(C*H*$_3$)$_2$), 1.31 (s, 3H, CH_3), 1.27 (dvt, $^3J_{H-H}$ = 7.5, *N* = 15.4, 6H, PCH(C*H*$_3$)$_2$), 1.05 (dvt, $^3J_{H-H}$ = 6.4, *N* = 12.5, 6H, PCH(C*H*$_3$)$_2$), 0.45 (m, 6H, PCH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, toluene-*d*$_8$, 298 K): δ 31.8 (d, $^1J_{Rh-P}$ = 133.2). IR (ATR, cm^{-1}): ν(C≡C) 1759 (w), ν(C=O) 1673 (s), ν(C-O) 1191 (s).

Preparation of Rh{(*E*)-C(CO$_2$Me)=C(CO$_2$Me)C$_6$H$_5$}{κ^3-P,O,P-[xant(P^{i}Pr$_2$)$_2$]} (7b)

A solution of **1b** (60 mg, 0.096 mmol) in toluene (3 mL) was treated with dimethyl acetylenedicarboxylate (12 μL, 0.098 mmol) and the resulting solution was stirred at room temperature for 8 h. The resulting solution was evaporated to dryness to afford an orange residue. Addition of pentane (4 mL) afforded an orange solid that was washed with further portions of pentane (5 x 4 mL) and dried in vacuo. Yield: 52 mg (70%). Anal. Calcd. for $C_{39}H_{51}O_5P_2Rh$: C, 61.25; H, 6.72. Found: C, 61.41; H, 6.73. HRMS (electrospray, *m*/*z*) calcd. for $C_{39}H_{51}O_5P_2Rh$ $[M]^+$: 764.2267; found: 764.2236. ^1H NMR (300.13 MHz, C_6D_6, 298 K): δ 9.43 (d, $J_{H\text{-}H}$ = 7.8, 2H, *o*-CH Ph), 7.24 (t, $J_{H\text{-}H}$ = 7.6, 2H, CH-arom POP), 7.16-7.02 (m, 3H, CH-arom POP, *p*-CH Ph), 6.97 (d, $J_{H\text{–}H}$ = 7.6, 2H, CH-arom POP), 6.80 (t, $J_{H\text{–}H}$ = 7.5, 2H, *m*-CH Ph), 3.82 (s, 3H, CO_2CH_3), 3.61 (s, 3H, CO_2CH_3), 3.05 (m, 2H, $PCH(CH_3)_2$), 2.18 (m, 2H, $PCH(CH_3)_2$), 1.39 (dvt, $^3J_{H\text{-}H}$ = 7.7, *N* = 16.3, 6H, $PCH(CH_3)_2$), 1.22 (dvt, $^3J_{H\text{-}H}$ = 7.7, *N* = 16.3, 6H, $PCH(CH_3)_2$), 1.18 (s, 3H, CH_3), 1.13-1.03 (m, 9H, 6H $PCH(CH_3)_2$ + 3H CH_3), 0.96 (dvt, $^3J_{H\text{-}H}$ = 7.6, *N* = 15.6, 6H, $PCH(CH_3)_2$). $^{13}C\{^1H\}$-apt NMR (75.48 MHz, C_6D_6, 298 K): δ 179.0 (dt, $^1J_{C\text{–}Rh}$ = 40.9, $^2J_{C\text{–}P}$ = 24.0, Rh-C), 175.9, 166.7 (both s, CO_2CH_3), 155.4 (vt, *N* = 15.0, C-arom POP), 141.8 (s, C Ph), 131.5 (s, CH-arom POP), 130.6 (s, C-arom POP), 129.9 (s, *o*-CH Ph), 128.7 (s, Rh-C=*C*), 128.5 (s, CH-arom POP), 127.1 (s, *m*-CH Ph), 125.3 (s, *p*-CH Ph), 124.2 (s, CH-arom POP), 123.6 (vt, *N* = 15.9, C-arom POP), 50.8, 50.1 (both s, CO_2CH_3), 34.6 (s, $C(CH_3)_2$), 33.7 (s, $C(CH_3)_2$), 32.0 (s, $C(CH_3)_2$), 24.8 (vt, *N* = 20.2, $PCH(CH_3)_2$), 24.5 (vt, *N* = 21.4, $PCH(CH_3)_2$), 20.2, 17.9, 16.6 (all s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6, 298 K): δ 36.7 (d, $^1J_{Rh\text{-}P}$ = 166.3). IR (ATR, cm^{-1}): ν(C=O) 1683 (s), 1664 (s), ν(C-O) 1198 (s).

Preparation of Rh{(*E*)-C(CO_2Me)=C(CO_2Me)(3-FC_6H_4)}{κ^3-P,O,P-[xant(P^iPr_2)$_2$]} (7d)

A solution of **1d** (80 mg, 0.12 mmol) in toluene (3 mL) was treated with dimethyl acetylenedicarboxylate (16 μL, 0.13 mmol) and the resulting solution was stirred at room temperature for 30 h. The resulting solution was evaporated to dryness to afford a yellow residue. Addition of pentane (4 mL) afforded an orange solid that was washed with further portions of pentane (5 x 4 mL) and dried in vacuo. Yield: 73 mg (75%). %). Anal. Calcd. for $C_{39}H_{50}FO_5P_2Rh$: C, 59.85; H, 6.44. Found: C, 59.46; H, 6.68. HRMS (electrospray, *m*/*z*) calcd. for $C_{39}H_{49}FO_5P_2Rh$ $[M - H]^+$: 781.2089; found: 781.2087. ^1H NMR (300.13 MHz, C_6D_6, 298 K): δ 9.93 (d, $J_{H\text{-}F}$ = 12.0, 1H, *o*-CH Ph), 8.82 (d, $J_{H\text{-}H}$ = 8.1, 1H, *o*-CH Ph), 7.07-6.97 (m, 5H, 4H CH-arom POP + 1H *m*-CH Ph), 6.82-6.73 (m, 3H, 2 CH-arom POP + 1H *p*-CH Ph), 3.79 (s, 3H, CO_2CH_3), 3.59 (s, 3H, CO_2CH_3), 3.01 (m, 2H, $PC\mathit{H}(CH_3)_2$), 2.13 (m, 2H, $PC\mathit{H}(CH_3)_2$), 1.36 (dvt, $^3J_{H\text{-}H}$ = 7.8, N = 16.1, 6H, $PCH(C\mathit{H}_3)_2$), 1.19 (dvt, $^3J_{H\text{-}H}$ = 7.8, N = 15.3, 6H, $PCH(C\mathit{H}_3)_2$), 1.18 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.07 (dvt, $^3J_{H\text{-}H}$ = 6.6, N = 12.6, 6H, $PCH(C\mathit{H}_3)_2$), 0.97 (dvt, $^3J_{H\text{-}H}$ = 7.2, N = 15.3, 6H, $PCH(C\mathit{H}_3)_2$). $^{13}C\{^1H\}$-apt NMR (75.48 MHz, C_6D_6, 298 K): δ 182.4 (dt, $^1J_{C\text{–}Rh}$ = 42.8, $^2J_{C\text{–}P}$ = 24.5, Rh-C), 175.8, 166.3 (both s, $\mathit{C}O_2CH_3$), 162.9 (d, $^1J_{C\text{-}F}$ = 240.2, C-F 3-FC_6H_4), 155.5 (vt, N = 14.6, C-arom POP), 144.3 (d, $^3J_{C\text{-}F}$ = 8.4, C 3-FC_6H_4), 131.5 (s, CH-arom POP), 130.7 (vt, N = 5.0, C-arom POP), 128.4 (s, CH-arom POP), 128.3 (s, Rh-C=*C*), 128.2 (s, *m*-CH 3-FC_6H_4), 125.7 (s, *o*-CH 3-FC_6H_4), 124.2 (s, CH-arom POP), 123.3 (vt, N = 17.8, C-arom POP), 116.3 (d, $^2J_{C\text{-}F}$ = 23.9, *o*-CH 3-FC_6H_4), 111.6 (d, $^2J_{C\text{-}F}$ = 21.6, *p*-CH 3-FC_6H_4), 50.9, 50.1 (both s, $CO_2\mathit{C}H_3$), 34.4 (s, $\mathit{C}(CH_3)_2$), 33.8, 32.4 (both s, $C(\mathit{C}H_3)_2$), 24.7 (dvt, $^2J_{C\text{–}Rh}$ = 2.1, N = 20.3, $P\mathit{C}H(CH_3)_2$), 24.5 (dvt, $^2J_{C\text{–}Rh}$ = 2.0, N = 19.2, $P\mathit{C}H(CH_3)_2$), 20.1 (vt, N = 6.6, $PCH(\mathit{C}H_3)_2$), 17.9 (vt, N = 8.9, $PCH(\mathit{C}H_3)_2$), 17.8, 16.6 (both s, $PCH(\mathit{C}H_3)_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 37.5 (d, $^1J_{Rh\text{-}P}$ = 165.2). IR (ATR, cm^{-1}): ν(C=O) 1684 (s), 1663 (s), ν(C-O) 1199 (s).

Supplementary Data.

Supplementary data (General information, crystallographic data, and IR and NMR spectra) are available with the article through the journal Web site.

Accession codes

CCDC 1959849, 1959850 and 1959851 contain the crystallographic data for this paper. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/products/csd/request/ (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk)).

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REFERENCES

(1) (a) Darensbourg, D. J.;Grötsch, G.; Wiegreffe, P.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3827. (b) Macgregor, S. A.; Roe, D. C.; Marshall, W. J.; Bloch, K. M.; Bakhmutov, V. I.; Grushin, V. V. *J. Am. Chem. Soc.* **2005**, *127*, 15304. (c) Raza, A. L.; Panetier, J. A.; Teltewskoi, M.; Macgregor, S. A.; Braun, T. *Organometallics* **2013**, *32*, 3795. (d) Kalläne, S. I.; Braun, T.; Braun, B.; Mebs, S. *Dalton Trans.* **2014**, *43*, 6786. (e) Kalläne, S. I.; Teltewskoi, M.; Braun, T.; Braun, B. *Organometallics* **2015**, *34*, 1156.

(2) (a) Segarra, C.; Mas-Marzá, E.; Lowe, J. P.; Mahon, M. F.; Poulten, R. C.; Whittlesey, M. K. *Organometallics* **2012**, *31*, 8584. (b) Schwartsburd, L.; Mahon, M. F.; Poulten, R. C.; Warren, M. R.; Whittlesey M. K. *Organometallics* **2014**, *33*, 6165.

(3) (a) Yamamoto, M.; Onitsuka, K.; Takahashi, S. *Organometallics* **2000**, *19*, 4669. (b) Walters, A. J. C.; Jellema, E.; Finger, M.; Aarnoutse, P.; Smits, J. M. M.; Reek, J. N. H.; de Bruin, B. *ACS Catal.* **2012**, *2*, 246.

(4) (a) Boyd, S. E.; Field, L. D.; Hambley, T. W.; Partridge, M. G. *Organometallics* **1993**, *12*, 1720. (b) Krug, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 1674. (c) Zámostná, L.; Sander, S.; Braun, T.; Laubenstein, R.; Braun, B.; Herrmann, R.; Kläring, P. *Dalton Trans.* **2015**, *44*, 9450.

(5) Lahoz, F. J.; Martin, E.; Tiburcio, J.; Torrens, H.; Terreros, P. *Trans. Met. Chem.* **1994**, *19*, 381.

(6) (a) Krug, C.; Hartwig, J. F. *Organometallics* **2004**, *23*, 4594. (b) Zhao, P.; Hartwig, J. F. *Organometallics* **2008**, *27*, 4749.

(7) Krug, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 2694.

(8) (a) Hahn, C.; Spiegler, M.; Herdtweck, E.; Taube, R. *Eur. J. Inorg. Chem.* **1998**, *1998*, 1425. (b) Hahn, C.; Spiegler, M.; Herdtweck, E.; Taube, R. *Eur. J. Inorg. Chem.* **1999**, *1999*, 435. (c) Kloek, S. M.; Heinekey, D. M.; Goldberg, K. I.. *Angew. Chem. Int. Ed.* **2007**, *46*, 4736. (d) Hanson, S. K.; Heinekey, D. M.; Goldberg, K. I. *Organometallics* **2008**, *27*, 1454. (e) Schwartsburd, L.; Iron, M. A.; Konstantinovski, L.; Ben-Ari, E.; Milstein, D. *Organometallics* **2011**, *30*, 2721. (f) Wang, Y.; Zheng, B.; Pan, Y.; Pan, C.; He, L.; Huang, K.-W.. *Dalton Trans.* **2015**, *44*, 15111. (g) Anaby, A.; Feller, M.; Ben-David, Y.; Leitus, G.; Diskin-Posner, Y.; Shimon, L. J. W.; Milstein; D. *J. Am. Chem. Soc.* **2016**, *138*, 9941. (h) Gair, J. J.; Qiu, Y.; Chan, N. H.; Filatov, A. S.; Lewis. J. C. *Organometallics* **2017**, *36*, 4699. (i) Zhou, C.; Hu, J.; Wang,

Y.; Yao, C.; Chakraborty, P.; Li, H.; Guan, C.; Huang M.-H.; Huang, K.-W. *Org. Chem. Front.* **2019**, *6*, 721. (j) Gair, J. J.; Qiu, Y.; Khade, R. L.; Chan, N. H.; Filatov, A. S.; Zhang, Y.; Lewis, J. C. *Organometallics* **2019**, *38*, 1407.

(9) (a) Esteruelas, M. A.; Oliván, M.; Vélez, A. *Organometallics* **2015**, *34*, 1911. (b) Esteruelas, M. A.; Oliván, M.; Vélez, A. *J. Am. Chem. Soc.* **2015**, *137*, 12321. (c) Curto, S. G.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; Vélez, A. *Organometallics* **2017**, *36*, 114. (d) Adams, G. M.; Colebatch, A. L.; Skornia, J. T.; McKay, A. I.; Johnson, H. C.; Lloyd-Jones, G. C.; Macgregor, S. A.; Beattie, N. A.; Weller, A. S. *J. Am. Chem. Soc.* **2018**, *140*, 1481.

(10) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 10236.

(11) (a) Esteruelas, M. A.; Nolis, P.; Oliván, M.; Oñate, E.; Vallribera, A.; Vélez, A. *Inorg. Chem.* **2016**, *55*, 7176. (b) Esteruelas, M. A.; Fernández, I.; García-Yebra, C.; Martín, J.; Oñate, E. *Organometallics* **2017**, *36*, 2298-2307. (c) Esteruelas, M. A.; García-Yebra, C.; Martín, J.; Oñate, E. *ACS Catal.* **2018**, *8*, 11314. (d) Esteruelas, M. A.; Oliván, M. In *Pincer Compounds: Chemistry and Applications*, 1st ed.; Morales-Morales, D., Ed.; Elsevier: Amsterdam, **2018**; chapter 16, p. 341. (e) Antiñolo, A.; Esteruelas, M. A.; García-Yebra, C.; Martín, J.; Oñate, E.; Ramos, A. *Organometallics* **2019**, *38*, 310. (f) Esteruelas, M. A.; Fernández, I.; García-Yebra, C.; Martín, J.; Oñate, E. *Inorg. Chem.* **2019**, *58*, 2265. (g) Esteruelas, M. A.; Fernández, I.; Martínez, A.; Oliván, M.; Oñate, E.; Vélez, A. *Inorg. Chem.* **2019**, 58, 4712.

(12) Esteruelas, M. A.; Oliván, M., in *Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Four Volumes* 3rd Edition (B. Cornils, W. A. Herrmann, M. Beller, R. Paciello, Eds), Wiley, **2017**; chapter 23, 1307-1332.

(13) Alonso, D. A.; Nájera, C.; Pastor, I. M.; Yus, M. *Chem. Eur. J.* **2010**, *16*, 5274.

(14) Yang, L.; Huang, H. *Chem. Rev.* **2015**, *115*, 3468.

(15) (a) Yamamoto, Y. *Chem. Soc. Rev.* **2014**, *43*, 1575. (b) Boyarskiy, V. P.; Ryabukhin, D. S.; Bokach, N. A.; Vasilyev, A. V. *Chem. Rev.* **2016**, *116*, 5894.

(16) (a) McGinnety, J. A.; Payne, N. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 6301. (b) Nolte, M. J.; Singleton, E. *Acta Crystallogr., Sect. B* **1975**, *31*, 2223. (c) Nolte, M. J.; Singleton, E. *Acta Crystallogr., Sect. B* **1976**, *32*, 1410. (d) Bianchini, C.; Mealli, C.; Meli, A.; Proserpio, D. M.; Peruzzini, M.; Vizza, F.; Frediani, P. *J. Organomet. Chem.* **1989**, *369*, C6. (e) Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A.; Scapacci, G. *J. Chem. Soc., Dalton Trans.* **1992**, 3371. (f) Lindner, E.; Wang, Q.; Mayer, H. A.; Fawzi, R.; Steimann, M. D. *J. Organomet. Chem.* **1993**, *453*, 289. (g) Osakada, K.; Hataya, K.; Yamamoto, T. *Inorg. Chem.* **1993**, *32*, 2360. (h) Vigalok, A.; Shimon, L. J. W.; Milstein, D. *Chem. Commun.* **1996**, 1673. (i) Takahashi, Y.; Hashimoto, M.; Hikichi, S.; Akita, M.; Moro-oka, Y. *Angew. Chem. Int. Ed.* **1999**, *38*, 3074. (j) Nicasio, M. C.; Paneque, M.; Pedro J. Pérez, P. J.; Pizzano, A.; Poveda, M. L.; Rey, L.; Sirol, S.; Taboada, S.; Trujillo, M.; Monge, A.; Ruiz, C.; Carmona, E. *Inorg. Chem.* **2000**, *39*, 180. (k) Argouarch, G.; Samuel, O.; Riant, O.; Daran, J.-C.; Kagan, H. B. *Eur. J. Org. Chem.* **2000**, 2893. (l) Paneque, M.; Sirol, S.; Trujillo, M.; Carmona, E.; Gutiérrez-Puebla, E.; Monge, M. A.; Ruiz, C.; Malbosc, F.; Serra-Le Berre, C.; Kalck, P.; Etienne, M.; Daran, J. C. *Chem. Eur. J.* **2001**, *7*, 3868. (m) Vicente, J.; Gil-Rubio, J.; Guerrero-Leal, J.; Bautista, D. *Organometallics* **2004**, *23*, 4871. (n) Ahijado, M.; Braun, T.; Noveski, D.; Kocher, N.; Neumann, B.; Stalke, D.; Stammler, H.-G. *Angew. Chem. Int. Ed.* **2005**, *44*, 6947. (o) Bleeke, J. R.; Shokeen, M.; Wise, E. S.; Rath, N. P. *Organometallics* **2006**, *25*, 2486. (p) Yu, X.-Y.; Patrick, B. O.; James, B. R.

Organometallics **2006**, *25*, 4870. (q) Carlton, L.; Mokoena, L. V.; Fernandes, M. A. *Inorg. Chem.* **2008**, *47*, 8696. (r) Penner, A.; Schröder, T.; Braun, T.; Ziemer, Z. *Eur. J. Inorg. Chem.* **2009**, 4464. (s) Penner, A.; Braun, T. *Eur. J. Inorg. Chem.* **2011**, 2579. (t) Meier, G.; Braun, T. *Angew. Chem. Int. Ed.* **2011**, *50*, 3280. (u) Hounjet, L. J.; McDonald, R.; Ferguson, M. J.; Cowie, M. *Inorg. Chem.* **2011**, *50*, 5361. (v) Teets, T. S.; Nocera, D. G. *Inorg. Chem.* **2012**, *51*, 7192. (w) Nakajima, T.; Sakamoto, M.; Kurai, S.; Kure, B.; Tanase, T. *Chem. Commun.* **2013**, *49*, 5250. (x) Cheung, W.-M.; Chiu, W.-H.; Sung, H. H. Y.; Williams, I. D.; Leung; W.-H. *Eur. J. Inorg. Chem.* **2014**, *2014*, 2961. (y) Halbach, R. L.; Teets, T. S.; Nocera, D. G. *Inorg. Chem.* **2015**, *54*, 7335.

(17) (a) Cipot-Wechsler, J.; Covelli, D.; Praetorius, J. M.; Hearns, N.; Zenkina, O. V.; Keske, E. C.; Wang, R.; Kennepohl, P.; Crudden, C. M. *Organometallics* **2012**, *31*, 7306. (b) Palacios, L.; Di Giuseppe, A.; Castarlenas, R.; Lahoz, F. J.; Pérez-Torrente, J. J.; Oro, L. A. *Dalton Trans.* **2015**, *44*, 5777.

(18) (a) Frech, C. M.; Shimon, L. J. W.; Milstein, D. *Helv. Chim. Acta* **2006**, *89*, 1730. (b) Verat, A. Y.; Fan, H.; Pink, M.; Chen, Y.-S.; Caulton, K. G. *Chem. Eur. J.* **2008**, *14*, 7680. (c) Praetorius, J. M.; Allen, D. P.; Wang, R.; Webb, J. D.; Grein, F.; Kennepohl, P.; Crudden, C. M. *J. Am. Chem. Soc.* **2008**, *130*, 3724. (d) Zenkina, O. V.; Keske, E. C.; Wang, R.; Crudden, C. M. *Angew. Chem. Int. Ed.* **2011**, *50*, 8100. (e) Hayashi, Y.; Szalda, D. J.; Grills, D. C.; Hanson, J. C.; Huang, K.-W.; Muckerman, J. T.; Fujita, E. *Polyhedron* **2013**, *58*, 106. (f) Keske, E. C.; Zenkina, O. V.; Asadi, A.; Sun, H.; Praetorius, J. M.; Allen, D. P.; Covelli, D.; Patrick, B. O.; Wang, R.; Kennepohl, P.; James; B. R.; Crudden, C. M. *Dalton Trans.* **2013**, *42*, 7414. (g) Kleinhans, G.; Guisado-Barrios, G.; Liles, D. C.; Bertrand, G.; Bezuidenhout, D. I. *Chem. Commun.* **2016**, *52*, 3504. (h) Palacios, L.; Meheut, Y.; Galiana-Cameo, M.; Artigas, M. J.; Di

Giuseppe, A.; Lahoz, F. J.; Polo, V.; Castarlenas, R.; Pérez-Torrente, J. J.; Oro, L. A. *Organometallics* **2017**, *36*, 2198-2207.

(19) (a) Bennett, M. J.; Donaldson, P. B. *J. Am. Chem. Soc.* **1971**, *93*, 3307. (b) Bennett, M. J.; Donaldson, P. B. *Inorg. Chem.* **1977**, *16*, 1585.

(20) Tejel, C.; Ciriano, M. A.; Jiménez, S.; Passarelli, V.; López, J. A. *Angew. Chem. Int. Ed.* **2008**, *47*, 2093.

(21) Ahrens, T.; Ahrens, M.; Braun, T.; Braun, B.; Herrmann, R. *Dalton Trans.* **2016**, *45*, 4716.

(22) Miyaji, T.; Kujime, M.; Hikichi, S.; Moro-oka, Y.; Akita, M. *Inorg. Chem.* **2002**, *41*, 5286.

(23) Esteruelas, M. A.; García-Yebra, C.; Martín, J.; Oñate, E. *Inorg. Chem.* **2017**, *56*, 676.

(24) See for example: (a) Pregosin, P. S.; Kumar, P. G. A.; Fernández, I. *Chem. Rev.* **2005**, *105*, 2977. (b) Barberá, J.; Puig, L.; Romero, P.; Serrano, J. L.; Sierra, T. *J. Am. Chem. Soc.* **2006**, *128*, 4487.

(25) (a) Esteruelas, M. A.; Oliván, M.; Vélez, A. *Inorg. Chem.* **2013**, *52*, 5339. (b) Esteruelas, M. A.; Oliván, M.; Vélez, A. *Inorg. Chem.* **2013**, *52*, 12108. (c) Curto, S. G.; de las Heras, L. A.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2019**, *38*, 3074.

(26) (a) Curto, S. G.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; Vélez, A. *Organometallics* **2018**, *37*, 1970. (b) Curto, S. G.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2019**,

38, 2062. (c) Curto, S. G.; Esteruelas, M. A.; Oliván, O.; Oñate, E. *Organometallics* **2019**, *38*, 4183.

(27) A *mer*-κ^3-P,O,P-coordination should give rise to doublets of virtual triplets.

(28) A square-planar pyramid with a *fac*-κ^3-P,O,P-coordination of the diphosphine does not allow equivalent P^iPr_2 groups.

(29) In principle, a similar structure with the dioxygen ligand disposed *trans* to the oxygen atom of the diphosphine could be also possible. However, it is little probable because in such disposition the three oxygen atoms of the molecule should compete by the same metal orbital.

(30) Bakhmutov, V. I.; Bozoglian, F.; Gómez, K.; González, G.; Grushin, V. V.; Macgregor, S. A.; Martin, E.; Miloserdov, F. E.; Novikov, M. A.; Panetier, J. A.; Romashov, L. V. *Organometallics* **2012**, *31*, 1315.

(31) Jover, J.; Miloserdov, F. M.; Benet-Buchholz, J.; Grushin, V. V.; Maseras, F. *Organometallics* **2014**, *33*, 6531.

(32) The carbonylation of **4a** to give **5a** is so fast that prevented isolation of **4a** in pure form. As a consequence a mixture of **4a** and **5a** in a ratio 65:35was obtained (see Experimental).

(33) Werner, H. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 927.

(34) Rosini, G. P.; Boese, W. T.; Goldman, A. S. *J. Am. Chem. Soc.* **1994**, *116*, 9498.

(35) Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E. *Organometallics* **1998**, *17*, 3141.

(36) (a) Braun, T.; Noveski, D.; Neumann, B.; Stammler, H.-G. *Angew. Chem. Int. Ed.* **2002**, *41*, 2745. (b) Itazaki, M.; Yoda, C.; Nishihara, Y.; Osakada, K. *Organometallics* **2004**, *23*, 5402. (c) Kumazawa, S.; Rodriguez Castanon, J.; Onishi, N.; Kuwata, K.; Shiotsuki, M.; Sanda, F. *Organometallics* **2012**, *31*, 6834. (d) Onishi, N.; Shiotsuki, M.; Masuda, T.; Sano, N.; Sanda, F. *Organometallics* **2013**, *32*, 846.

Table 1. Diffusion Coefficients (*D*) and Hydrodynamic Radii (R_H) Obtained from C_6D_6[a] Solutions of 1b-d and CD_2Cl_2[b] Solutions of 2b-d.[a]

Complex	*D* (10^{-10} m^2 s^{-1})	R_H (Å)[c]
1b	5.99	5.18
1c	6.54	4.74
1d	6.47	4.79
2b	10.6	4.70
2c	10.5	4.75
2d	10.5	4.74

[a] Viscosity at 293 K, 0.69 mPa·s. [b] Viscosity at 293 K, 0.43 mPa·s. [c] Calculated using the Stokes-Einstein equation.

Figure Captions:

Scheme 1. Synthesis of P,N,P-rhodium aryl complexes.

Scheme 2. Synthesis of P,O,P-rhodium aryl complexes.

Figure 1. Molecular diagram of complex **2a** (ellipsoids shown at 50% probability). All hydrogen atoms are omitted for clarity. Selected bond distances (A) and angles (deg): Rh-P(1) = Rh(A)-P(1A) = 2.3725(15), Rh-P(2) = Rh(A)-P(2A) = 2.4075(15), Rh-O(1) = Rh(A)-O(1A) = 1.988(4), Rh(A)-O(2) = Rh-O(2A) = 2.024(4), Rh-O(2) = Rh(A)-O(2A) = 2.439(3), Rh-C(1) = Rh(A)-C(1A) = 2.016(5), O(1)-O(2) = O(1A)-O(2A) = 1.442(5); P(1)-Rh-P(2) = P(1A)-Rh(A)-P(2A) 103.59(5), C(1)-Rh-O(2) = C(1A)-Rh(A)-O(2A) = 132.7(17).

Scheme 3. Reaction of **1** with dioxygen.

Scheme 4. Rupture of the double peroxide bridge.

Scheme 5. Reactions of **1** with carbon monoxide.

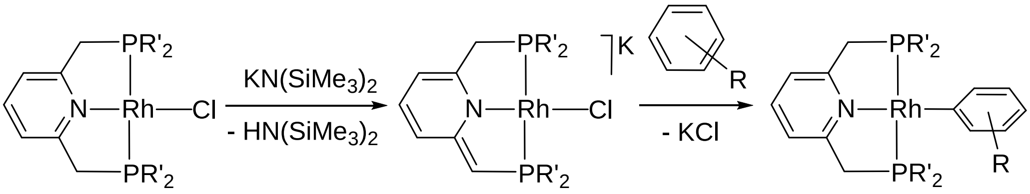
Figure 2. Molecular diagram of complex **4d** (ellipsoids shown at 30% probability). All hydrogen atoms are omitted for clarity. Selected bond distances (A) and angles (deg): Rh-P(1) = Rh-P(1A) = 2.287(2), Rh-C(1) = 2.145(14), Rh-C(7) = 1.816(17); P(1)-Rh-P(1A) = 149.37(10), C(1)-Rh-C(7) = 161.2(5), P(1)-Rh-C(7) = 95.20(12), P(1)-Rh-C(1) = 89.67(11).

Scheme 6. Insertion of dimethyl acetylenedicarboxylate into Rh-aryl bonds.

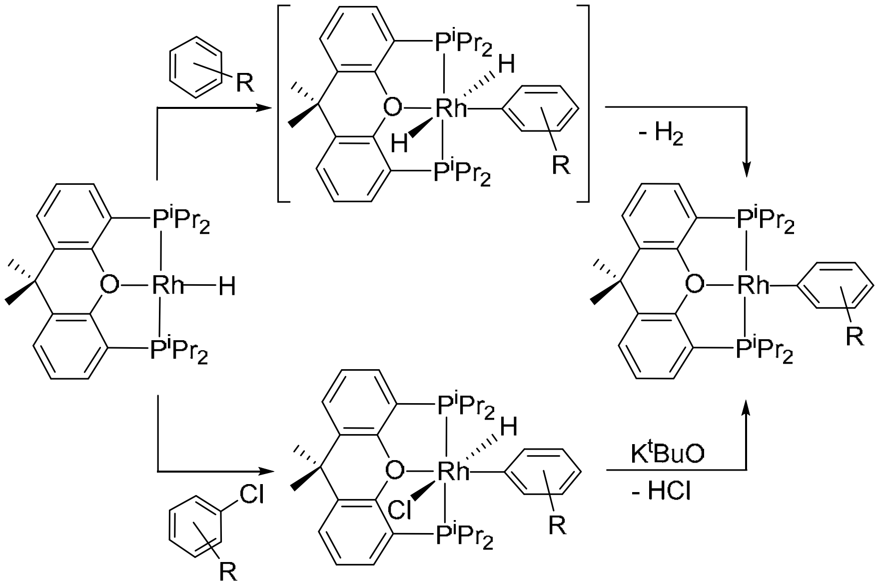
Figure 3. Molecular diagram of complex **7b** (ellipsoids shown at 50% probability). All hydrogen atoms are omitted for clarity. Selected bond distances (A) and angles (deg): Rh-P(1) = 2.2809(11), Rh-P(2) = 2.2851(10), Rh-C(1) = 1.976(4), C(1)-C(2) = 1.372(5); P(1)-Rh-P(2) =

159.33(4), C(1)-Rh-O(5) = 177.64(12), P(1)-Rh-C(1) = 99.22(11), P(2)-Rh-C(1) = 96.85(11), P(1)-Rh-O(5) = 81.57(7), P(2)-Rh-O(5) = 81.89(7).

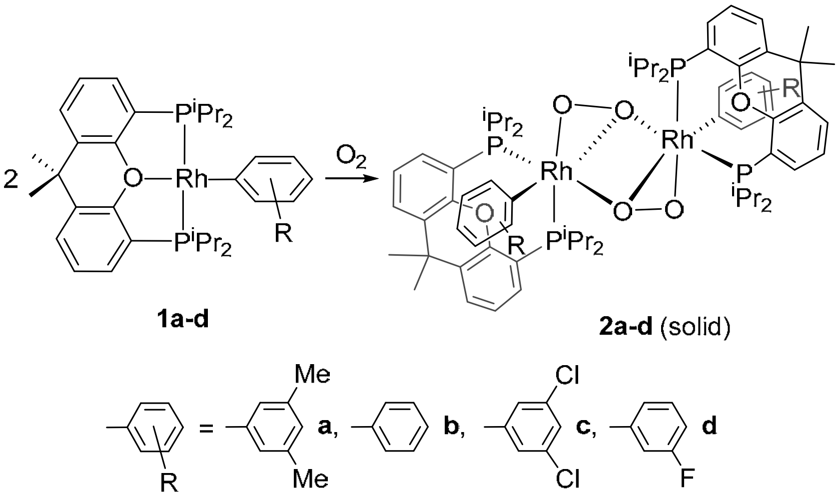
Scheme 1



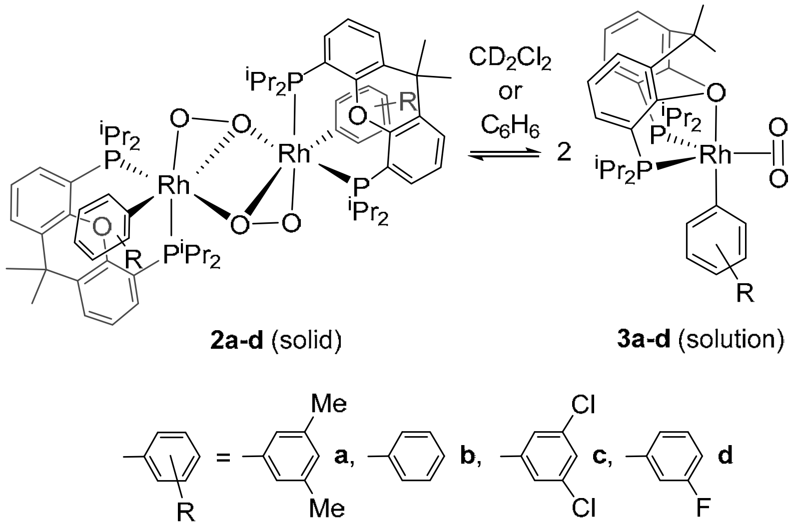
Scheme 2



Scheme 3



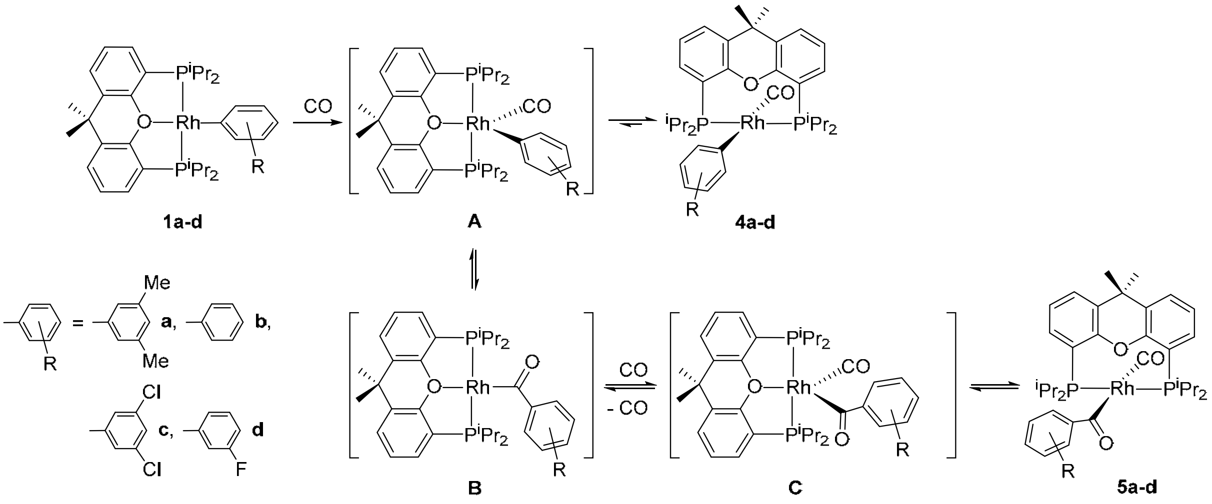
Scheme 4



2a-d (solid)

3a-d (solution)

Scheme 5



Scheme 6

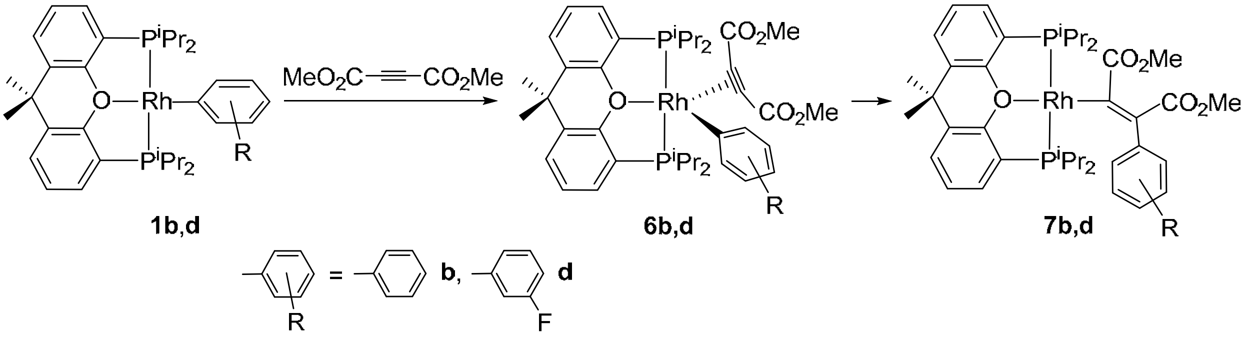


Figure 1

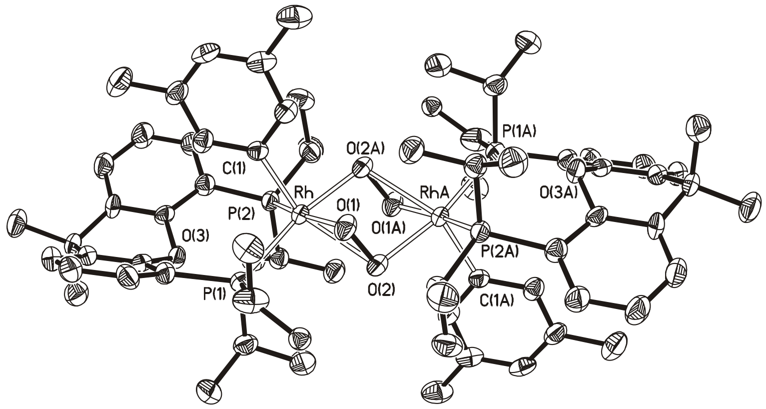


Figure 2

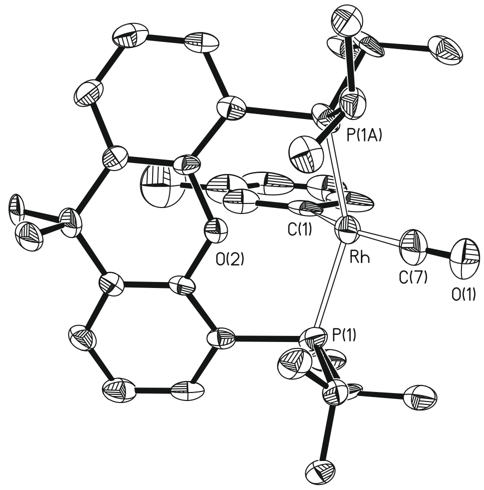
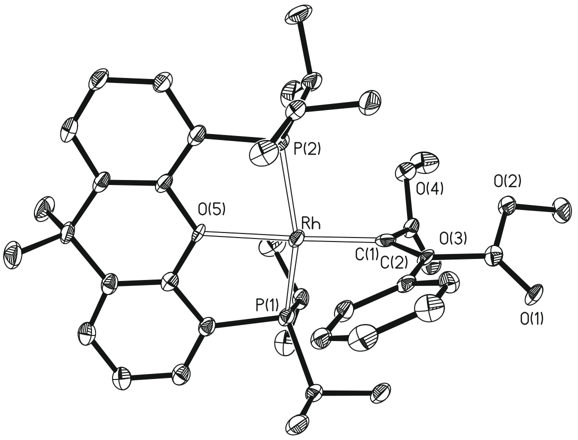


Figure 3



Graphical abstract