Rhodium(III) Acyl Hydrido, Acyl Hydroxyalkyl, Diacyl, Acyl Hydrido Aldehyde, and Acyl Hydrido Alcohol Complexes. Reduction of Aldehyde to Alcohol through Rhodium Hydroxyalkyl Complexes

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$[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) reacts with *o*-(diphenylphosphino)benzaldehyde (PPh_2-(o-C_6H_4CHO)) (Rh/P = 1:1) in the presence of pyridine to give an acyl hydrido species, [RhHCl(PPh_2-(o-C_6H_4CO))$(py)_2$] (**1**). In chlorinated solvents exchange of hydride by chloride gives [$RhCl_2$(PPh_2(o-C_6H_4CO))$(py)_2$] (**2**). The reactions of **1** with PPh_3 and of **2** with biacetyl dihydrazone (bdh) gives the pyridine substitution products [RhHCl(PPh_2(o-C_6H_4CO))(PPh_3)(py)] (**4**) and [$RhCl_2$(PPh_2(o-C_6H_4CO))-(bdh)] (**3**), respectively. By using a 1:2 ratio of Rh to PPh_2(o-C_6H_4CHO) [RhHCl(PPh_2(o-C_6H_4CO))(κ^1-PPh_2(o-C_6H_4CHO))(py)] (**5**) with trans phosphorus atoms is formed. The aldehyde group may undergo two different reactions. In benzene **5** affords the acyl hydroxyalkyl species [RhCl(PPh_2(o-C_6H_4CO))-(PPh_2(o-C_6H_4CHOH))(py)] (**6**) with cis phosphorus atoms, via a pyridine dissociation path. **6** undergoes dehydrogenation, with H_2 evolution, to afford the diacyl derivative [RhCl(PPh_2(o-C_6H_4CO))$_2$(py)] (**8**), which shows fluxional behavior in solution, with the values $\Delta H^{\ddagger} = 8.8 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -16.7 \pm 1$ eu. Opening of the acylphosphine chelate appears to be responsible for the fluxionality. In methanol **5** undergoes displacement of chloride by the aldehyde to afford the cationic acyl hydrido aldehyde [RhH(PPh_2(o-C_6H_4CO))(κ^2-PPh_2(o-C_6H_4CHO))(py)]$^+$ (**10**), which can be isolated if precipitated immediately with an appropriate counterion. Longer reaction periods of **5** in methanol solution lead to a mixture of the diacyl **8** and the cationic acyl hydrido alcohol [RhH(PPh_2(o-C_6H_4CO))(κ^2-PPh_2(o-C_6H_4-CH_2OH))(py)]$^+$ (**11**). The spectroscopic characterization of some intermediates in this reaction evidence a bimolecular ionic mechanism as being responsible for the hydrogenation of the aldehyde with the hydroxyalkyl **6** being the source of both proton and hydride. Complex **11** can also be obtained by the reaction of **5** with $NaBH_4$ in methanol solution.

Introduction

Organometallic rhodium complexes play an important role in the transformation of many organic compounds.[1,2] The catalytic hydrogenation of aldehydes or ketones is a key reaction in chemical syntheses. In their reduction to alcohols, and also in the conversion of syngas to methanol or ethylene glycol, alkoxy or hydroxyalkyl intermediates are believed to be involved.[3] Both alkoxy and hydroxyalkyl compounds are well-known for late transition metals.[4] The hydrogenation of aldehydes with molecular hydrogen in protic solvents and with rhodium complexes as catalysts has been reported to proceed via hydroxyalkyl intermediates.[5] The alkoxy species are believed to be involved in the H-transfer reduction of ketones or aldehydes with secondary alcohols promoted by rhodium derivatives,[6] though when the catalyst contains chiral diamine ligands recent theoretical studies[7] suggest that the enantioselectivity of the reaction is related to an outer-sphere hydrogen transfer mechanism similar to that operating in ketone hydrogenations catalyzed by ruthenium diamine compounds.[8] Metallohydroxyalkyl complexes are generally prepared as kinetic products from the reaction of metallocarbonyl or metalloacyl species with reducing agents, and when they are unstable, a frequent decomposition path involves their dissociation into

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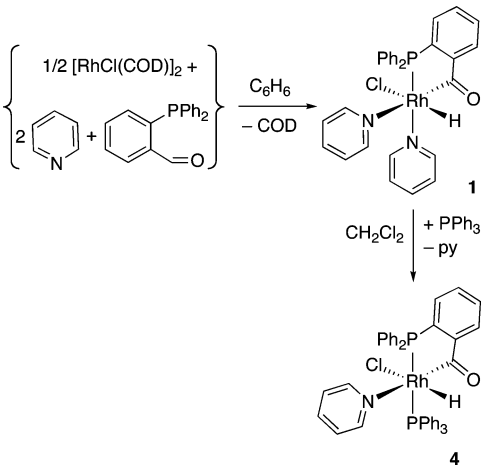
metal hydride and aldehyde units.[9] Therefore, the insertion of an aldehyde into an M−H bond to afford hydroxyalkyls is rarely observed.[4c,10] Rhodium hydride complexes containing porphyrins, $RhH(N_4)$, and showing some acidic character react with RCHO to give the hydroxyalkyl derivatives $Rh(CH(OH)R)(N_4)$.[9,11] Also, chelate assistance has been used to stabilize the hydroxyalkyl derivative $Mn(CO)_4(PPh_2(o\text{-}C_6H_4CHOH))$, formed by insertion of *o*-(diphenylphosphine)benzaldehyde ($PPh_2(o\text{-}C_6H_4CHO)$) into the M−H bond of $HMn(CO)_5$.[12] The course of the reaction between $PPh_2(o\text{-}C_6H_4CHO)$ and metal hydride derivatives depends markedly on the metal and also on the coligands present in the complex undergoing the reaction. Thus, $PtH(PPh_2O)(PPh_2OH)_2$ gives the cyclic platinum alkoxide $Pt(PPh_2O)(PPh_2OH)(PPh_2(o\text{-}C_6H_4CH_2O))$.[13] Neutral complexes such as $[IrHCl(PPh_2(o\text{-}C_6H_4CO))(CO)(\kappa^1\text{-}PPh_2(o\text{-}C_6H_4CHO))]$, containing a P-coordinated $PPh_2(o\text{-}C_6H_4CHO)$ ligand, or $[RhHCl(PPh_2(o\text{-}C_6H_4CO))(\kappa^2\text{-}PPh_2(o\text{-}C_6H_4CHO))]$, containing a chelating P-aldehyde $PPh_2(o\text{-}C_6H_4CHO)$ ligand, have not been reported to undergo any insertion reaction,[14] and cationic rhodium derivatives containing a P-coordinated $PPh_2(o\text{-}C_6H_4CHO)$ ligand and chelating diimines (NN) such as $[RhH(PPh_2(o\text{-}C_6H_4CO))(\kappa^1\text{-}PPh_2(o\text{-}C_6H_4CHO))(NN)]^+$ undergo the insertion reaction to afford the hydroxyalkyl derivatives $[Rh(PPh_2(o\text{-}C_6H_4CO))(PPh_2(o\text{-}C_6H_4CHOH))(NN)]^+$.[15]

In this work we report the reactions of the rhodium(I) compound $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) with $PPh_2(o\text{-}C_6H_4CHO)$ in the presence of pyridine to yield different products that include acyl hydrido complexes formed by oxidative addition of aldehyde, acyl hydroxyalkyl species formed by insertion of aldehyde into the Rh−H bond, a diacyl derivative formed by dehydrogenation of the acyl hydroxyalkyl species, and an acyl hydrido aldehyde complex that can be hydrogenated to the corresponding acyl hydrido alcohol compound. Experimental evidence for an ionic hydrogenation mechanism of aldehyde involving proton and hydride transfer furnished by the acyl hydroxyalkyl species is also provided.

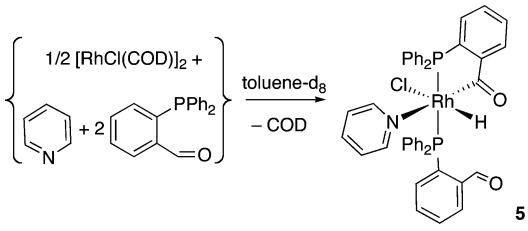
Results and Discussion

The reaction of $[RhCl(COD)]_2$ with $PPh_2(o\text{-}C_6H_4CHO)$ (Rh:P = 1:1) in the presence of pyridine (py) leads to the acyl hydrido derivative $[RhHCl(PPh_2(o\text{-}C_6H_4CO))(py)_2]$ (**1**) with displacement of 1,5-cyclooctadiene, as shown in Scheme 1. This reaction is in line with the well-known ability of the aldehyde−phosphine ligand to promote the chelate-assisted oxidative addition of the aldehyde to late-transition-metal complexes.[16] Complex **1** shows the expected spectroscopic features. The $^{31}P\{^1H\}$ NMR spectrum contains only one doublet at the characteristic low field due to the five-membered-ring effect,[17] and the ^1H NMR spectrum shows a doublet of doublets in the high-field region, at −15.93 ppm, consistent with a hydride cis to phosphorus ($J(P,H) = 18$ Hz) and trans to chloride.[18] Complex **1** shows low stability in chlorinated solvents, and in chloroform exchange of hydride by chloride occurs to afford the complex $[RhCl_2(PPh_2(o\text{-}C_6H_4CO))(py)_2]$ (**2**), as shown by the appearance of a resonance at 5.30 ppm due to formation of dichloromethane when the reaction is performed in $CDCl_3$. Such a reaction has several precedents.[19] Complex **2** reacts with the chelating diimine biacetyl dihydrazone ($H_2NN{=}C(CH_3)C(CH_3){=}NNH_2$, bdh), which displaces pyridine to afford $[RhCl_2(PPh_2(o\text{-}C_6H_4CO))(bdh)]$ (**3**). The $^{31}P\{^1H\}$ NMR spectra of **2** and **3** are very similar; therefore, we believe that in **2** both pyridine ligands are mutually cis.

Scheme 1



Complex **1** reacts also with triphenylphosphine, which displaces one pyridine ligand to afford the complex $[RhHCl(PPh_2(o\text{-}C_6H_4CO))(py)(PPh_3)]$ (**4**), as shown in Scheme 1. The hydride chemical shift (−14.55 ppm) and the $J(P,P)$ coupling constant (375 Hz) are characteristic of hydride trans to chloride and of two mutually trans phosphorus atoms. In accordance with this observation, the reaction of $[RhCl(COD)]_2$ with $PPh_2(o\text{-}C_6H_4CHO)$ (Rh:P = 1:2) in the presence of pyridine leads to the chelate−assisted oxidative addition of one phosphine−aldehyde ligand, with displacement of 1,5-cyclooctadiene, and to the coordination of the second phosphine−aldehyde ligand as a P-monodentate ligand to afford the neutral derivative $[RhHCl(PPh_2(o\text{-}C_6H_4CO))(\kappa^1\text{-}PPh_2(o\text{-}C_6H_4CHO))(py)]$ (**5**), similar to **4** and with a dangling aldehyde group, as shown in eq 1.



(1)

Complex **5** is extremely reactive and was identified only in solution (see the Experimental Section). Its free aldehyde group

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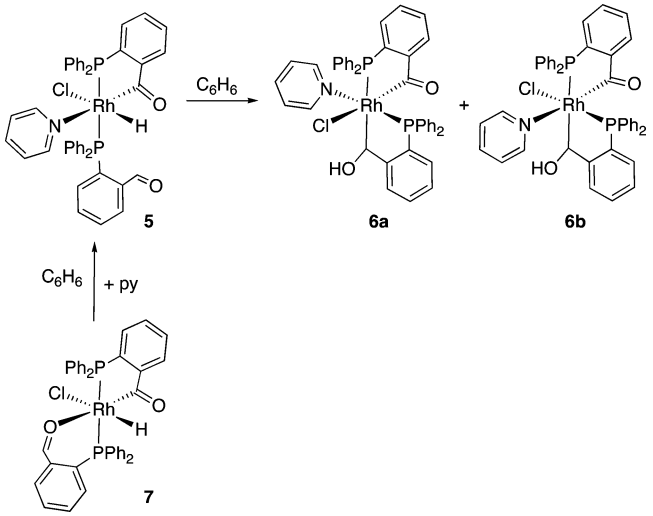
Scheme 2

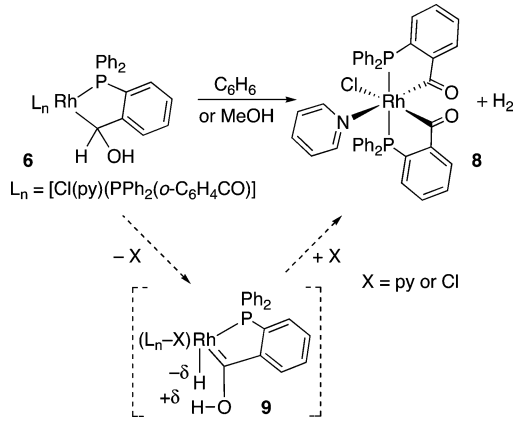


undergoes different reactions, including hydrogenation and dehydrogenation, depending on the reaction conditions.

Hydroxyalkyl Formation from Complex 5 and Its Subsequent Dehydrogenation. In benzene solution complex **5** reacts readily to afford the hydroxyalkyl derivative [RhCl(PPh_2-(*o*-C_6H_4CO))(PPh_2(*o*-C_6H_4CHOH))(py)] (**6**) (see Scheme 2), which is a mixture of the two isomers **6a** and **6b** in a 3:1 ratio. In line with previous observations,[10,11] this behavior suggests a certain acidic character of the hydride in complex **5**. The transformation of this acyl hydrido complex, also containing a dangling aldehyde group and two mutually trans phosphorus atoms, into acyl hydroxyalkyl derivatives with two mutually cis phosphorus atoms requires two different steps to occur, namely isomerization and insertion of the aldehyde into the Rh−H bond. By following the reaction in C_6D_6 by NMR, we observed that the presence of an excess of pyridine made the overall reaction slower. Thus, after 15 min, the ratio of **6** to **5** was 2:1 when using a Rh to py ratio of 1:1 while, when using a Rh to py ratio of 1:2, the ratio of **6** to **5** was only 1:2, as concluded from the $^{31}P\{^1H\}$ NMR spectra. Longer reaction periods led to the complete transformation of **5** into **6**. Former studies have shown that the formation of rhodium(III) acyl hydroxyalkyl derivatives from rhodium(III) acyl hydrido species is favored when the phosphorus atoms are mutually cis;[15a] therefore, our proposal is that the isomerization reaction occurs first, through a pyridine dissociation step, to afford a species with two mutually cis phosphorus atoms. Protonation of the aldehyde group by an acidic Rh−H can then afford the final product **6**. As shown in Scheme 2, compound **6** can be obtained, also as a 3:1 mixture of **6a** and **6b**, by the reaction of pyridine with an acyl hydrido complex containing a phosphine−aldehyde chelating ligand, [RhHCl(PPh_2(*o*-C_6H_4CO))(κ^2-PPh_2(*o*-C_6H_4-CHO))] (**7**),[14b] in which the hydroxyalkyl formation reaction is not observed. Inspection of the in situ reaction performed in C_6D_6 by NMR indicates that the coordinated aldehyde group in **7** is displaced by pyridine to afford complex **5**, which then gives **6**. As has been previously observed,[15,20] N-donor ligands favor the hydroxyalkyl formation in rhodium hydrido complexes by migration of the hydride to the more nucleophilic oxygen atom of the aldehyde.

Compound **6** has been fully characterized by NMR, including 2D experiments. The obtained spectra confirm the formation

Scheme 3



of the hydroxyalkyl groups bonded to rhodium,[12,21] trans to the phosphorus atom of the acyl−phosphine chelate. The ^{13}C resonances appear in the 93−97 ppm range as doublets of doublets due to coupling with rhodium (J(Rh,C) = 22 Hz) and with a trans phosphorus atom (J(P,C) = 98 Hz). In the HSQC experiment, correlation of the resonance due to the major species with a resonance at 6.75 (C*H*OH) ppm is observed and this signal makes COSY with a resonance at 8.48 ppm (CHO*H*). In the ^1H NMR spectra the alkyl resonance is obscured by the phenyl rings and the hydroxy signal is clearly observed. The latter disappears upon addition of a few drops of CD_3OD, and its low-field appearance suggests some extent of hydrogen bond formation, most likely with the cis chloride ligand. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets of doublets for each isomer with mutually cis phosphines (J(P,P) = 20 Hz). Isomers **6a** and **6b** differ in the groups, chlorine or pyridine, trans to acyl and to phosphorus of the hydroxyalkyl−phosphine chelate. When the electronic effects are taken into account, higher stability for a species where the best σ-donor is trans to the poorer σ-donor can be expected.[22] According to this, the major isomer **6a** should contain the lowest trans effect ligand, chlorine, trans to the acyl group, whose trans effect is almost as high as that of hydride.[23] The ^{31}P resonances of the hydroxyalkyl−phosphine chelate appear around 54 ppm, and the coupling constant J(Rh,P), lower for the major isomer **6a** (155 Hz) than for the minor isomer **6b** (160 Hz), is in line with the phosphorus being trans to the pyridine nitrogen with higher trans effect in **6a**.[24]

Compound **6** has low stability in benzene or in chloroform solution, so that after 24 h it is completely transformed into the diacyl derivative [RhCl(PPh_2(*o*-C_6H_4CO))$_2$(py)] (**8**) (see Scheme 3) with hydrogen loss, as evidenced by the appearance of a small resonance at 4.63 ppm in the ^1H NMR spectra of a $CDCl_3$ solution of **6**.[25] In methanol the reaction is faster and **6** is completely transformed into **8** in ca. 45 min. Complex **6** shows lower stability than the related compound [Rh(PPh_2(*o*-C_6H_4-CO))(PPh_2(*o*-C_6H_4CHOH))(bdh)]BPh_4,[15a] containing a better donor ligand such as the bidentate diimine instead of pyridine and chloride. This is not surprising,[12a] but the usual decomposition paths reported for hydroxyalkyl complexes include regeneration of the M−H bond and free aldehyde or, if an acid is

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added, disproportionation with hydride transfer to yield an acyl and an alkyl complex.[12,21] No presence of **5** was observed in the NMR spectra recorded during the transformation of **6** into **8**, thus excluding the reversal of **6** into **5**.

We were unable to detect any intermediate during the dehydrogenation reaction, but as an unusual mechanism appears to operate in this reaction, we considered the possibility of a ligand dissociation step, which would decrease the electronic density on the metal and the stability of the hydroxyalkyl[10] and would allow transfer of α-hydrogen from carbon to rhodium to give an intermediate such as the hydrido hydroxycarbene **9** depicted in Scheme 3. Although not frequent for late-transition-metal complexes, α-H elimination to give hydridocarbene species is known.[26] Iridium hydroxycarbene complexes obtained from the reaction of iridium compounds with aldehydes[27] or hydrido hydroxycarbene derivatives formed by protonation of iridium hydrido formyl derivatives[28] have been reported. Also, hydrido hydroxycarbene formation has been shown to operate in the decarbonylation of aldehydes by $[RuH(Cl)(P^iPr_3)_2]_2$[29] and in the hydrocarbonylation of olefins, leading to alcohols[30] or, in the reaction of CO with ethene, to give pentan-3-one[31] using rhodium trialkylphosphine complexes in protic solvents. The interaction of the hydride, behaving as a proton acceptor,[29,32] with the alcoholic proton in intermediate **9** would give complex **8** with hydrogen loss. This mechanism would also explain the overall reaction being faster in methanol, where chloride dissociation is easy. The described hydroxyalkyl formation and its dehydrogenation would involve rhodium(III) hydrido derivatives that behave as proton donors (complex **5**) or as hydride donors (species **9**). Both modes of reactivity are now well established for transition-metal hydrides, and recently the ability of the palladium hydride $[PdH(dppe)_2]^+$ to transfer a hydride or a proton to carbocations or carboanions, respectively, has been reported.[33] We believe that other evidence reported later in this work point to the formation of hydrido hydroxycarbene species from **6**.

Complex **8** is prepared in better yield by reaction of $[RhCl(COD)]_2$ with $PPh_2(o\text{-}C_6H_4CHO)$ in the presence of pyridine in methanol (see the Experimental Section) and has been fully characterized by NMR. At 253 K its $^{31}P\{^1H\}$ NMR spectrum shows an ABX spin pattern with $J(P,P) = 336$ Hz, indicating the trans disposition of both phosphorus atoms, while the $^{13}C\{^1H\}$ NMR spectrum shows in the low-field region, at ca. 230 ppm, two doublets due to two inequivalent acyl groups trans to chloride and pyridine, respectively. Complex **8** is fluxional in solution, as shown by inspection of the $^{31}P\{^1H\}$ NMR spectra. Due to **8** being insoluble in toluene-d_8, the spectra were obtained from $CDCl_3$ solutions in the 253−328 K range. When the temperature is raised, the signals due to the ABX pattern broaden and coalescence occurs near 330 K (see Figure 1). From line-shape analysis[34] of the variable-temperature $^{31}P\{^1H\}$ NMR spectra of complex **8**, the activation parameters $\Delta H^{\ddagger} = 8.8 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -16.7 \pm 1$ cal K^{-1} mol^{-1} have been determined. The entropy of activation is indicative of an intramolecular rearrangement responsible for the exchange of pyridine and chloride.[35] We believe that opening of the acyl−phosphine chelate can account for the observed fluxional behavior.

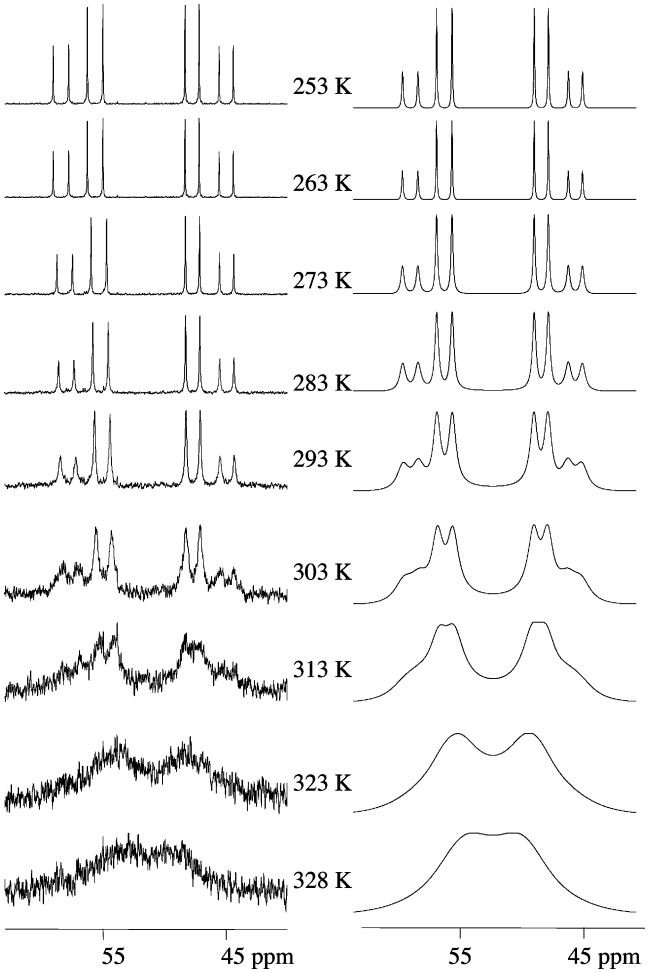

Figure 1. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **8** in $CDCl_3$: (left) experimental; (right) calculated.

An X-ray diffraction study of **8** confirms the structure depicted in Scheme 3. Selected bond distances and angles are listed in Table 1, and Figure 2 gives a molecular drawing. The geometry about the metal atom is distorted octahedral; the maximum deviation of 10.4° corresponds to the angle C20−Rh1−P1. Four positions are occupied by the phosphorus and carbon atoms of the two bidentate ligands, and the other two positions are occupied by the nitrogen atom of the pyridine and by chloride. Both phosphorus atoms are mutually trans, and the acyl groups are mutually cis. The distances comprising the chelate ligands are in the expected ranges,[15a,36] and we find some differences in the features of the acylphosphine ligands. The best least-squares plane for the Rh1, C20, C21, C22, and P2 atoms and the C21, C22, C24, C25, C26 plane are almost

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 8, Including the Hydrogen-Bond Geometry

Rh1−P2	2.300(1)	Rh1−P1	2.367 (1)
Rh1−N1	2.261(4)	Rh1−Cl1	2.521(1)
Rh1−C20	1.994(5)	Rh1−C(1)	2.002(5)
O2−C20	1.217(5)	O1−C1	1.206(5)
O3−H3	0.840	H3···O1	2.590
O3···O1	3.289(9)		
C20−Rh1−C1	88.6(2)	C20−Rh1−N1	90.6(2)
C1−Rh1−N1	174.3(2)	C20−Rh1−P2	84.8(1)
C1−Rh1−P2	90.4(1)	N1−Rh1−P2	95.1(1)
C20−Rh1−P1	100.6(1)	C1−Rh1−P1	81.3(1)
N1−Rh1−P1	93.4(1)	P2−Rh1−P1	170.0(4)
C20−Rh1−Cl1	174.3(1)	C1−Rh1−Cl1	92.0(1)
N1−Rh1−Cl1	89.3(1)	P2−Rh1−Cl1	89.5(4)
P1−Rh1−Cl1	85.1(4)	O3−H3···O1	141.9

coplanar, with a dihedral angle of 5.0(1)°, whereas the best least-squares plane for the Rh1, C1, C2, C3, and P1 atoms forms a dihedral angle of 20.8(1)° with the corresponding phenyl ring. Also, the Rh−P2 and Rh−P1 distances, 2.300(1) and 2.367(1) Å, respectively, are significantly different. These different features are probably due to the expected distortion of having two five-membered chelate rings. The presence of a solvent molecule, methanol, bonded to the oxygen atom O1 of an acyl group, can also have some influence in the observed features.

Hydroxyalkyl as Source of Proton and Hydride for the Hydrogenation of Coordinated Aldehyde. In methanol solution complex **5** reacts readily to undergo displacement of chloride by the aldehyde, affording the cationic acyl hydrido complex $[RhH(PPh_2(o\text{-}C_6H_4CO))(\kappa^2\text{-}PPh_2(o\text{-}C_6H_4CHO))(py)]^+$ (**10**), containing a phosphine−aldehyde chelate (see Scheme 4), as confirmed by following the in situ reaction in CD_3OD by NMR (vide infra). The isolation of **10** requires the immediate addition of a bulky anion salt such as $NaBPh_4$. [**10**]BPh_4 can thus be obtained in up to 80% yield.

The spectroscopic data allow its unambiguous characterization. As observed in other rhodium(III) aldehyde complexes,[16,37] the aldehyde coordination of $PPh_2(o\text{-}C_6H_4CHO)$ in **10** is the σ-aldehyde mode. The IR spectrum shows ν(C═O) absorptions at lower wavenumber than for the free ligand, and in the $^{13}C\{^1H\}$ NMR spectrum a resonance at slightly lower field than for the free aldehyde is observed. The ^1H NMR spectrum shows a sharp singlet at slightly higher field than for the free aldehyde, and the appearance of a resonance at −13.88 ppm indicates the presence of a hydride trans to nitrogen. A shift of the $^{31}P\{^1H\}$ resonance of the phosphine−aldehyde ligand in **5** toward higher field upon formation of **10** is in accordance with the presence of a six-membered ring,[17] and the J(P,P) coupling constant of 346 Hz agrees with a trans arrangement of the phosphorus atoms.

Complex **10**, prepared in situ in methanol solution, reacts with $NaBH_4$ to undergo the aldehyde hydrogenation, leading to the complex $[RhH(PPh_2(o\text{-}C_6H_4CO))(\kappa^2\text{-}PPh_2(o\text{-}C_6H_4CH_2\text{-}OH))(py)]^+$ (**11**), which contains a phosphine−alcohol chelate. Complex **11** was isolated as the perchlorate salt, [**11**]ClO_4, by addition of $NaClO_4$ and was characterized by spectroscopic means, including 2D experiments. The ^1H and $^{13}C\{^1H\}$ NMR spectra confirm the formation of the alcoholic group bonded to rhodium. Its ^{13}C resonance appears at 67.6 ppm as a doublet, most likely due to coupling with the P atom of the alcohol−phosphine chelate (J(P,C) = 7 Hz), and the ^1H resonances appear at 5.12 and 4.44 ppm as doublets of doublets for the methylene group and at 6.19 {t} ppm for the hydroxy group, which disappears upon addition of a few drops of CD_3OD. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets of doublets, and

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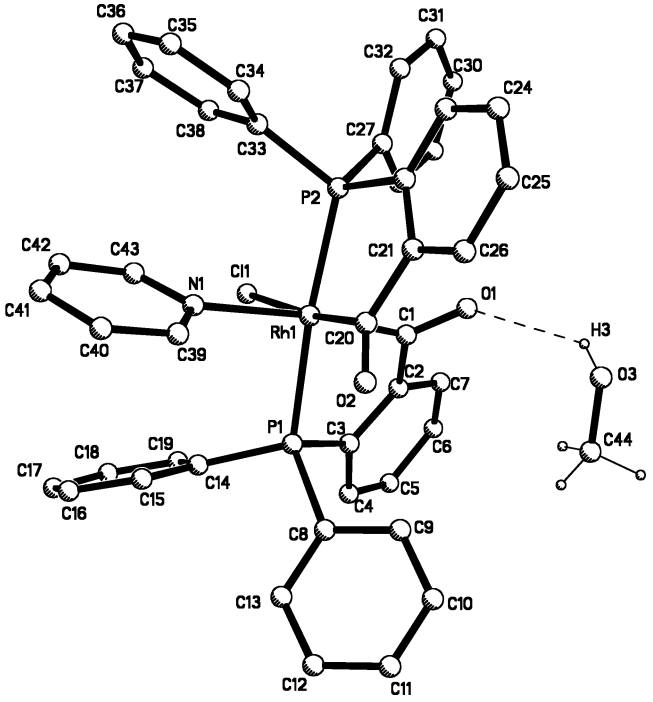
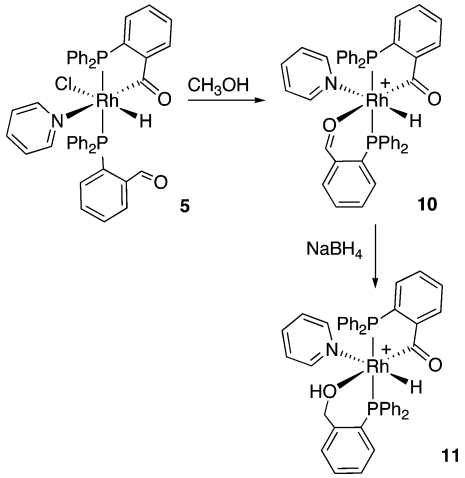


Figure 2. PLUTO view of complex **8** showing the atomic numbering and the intermolecular hydrogen bond. All but one of the hydrogen atoms and the labels of some C atoms have been omitted for clarity.

Scheme 4

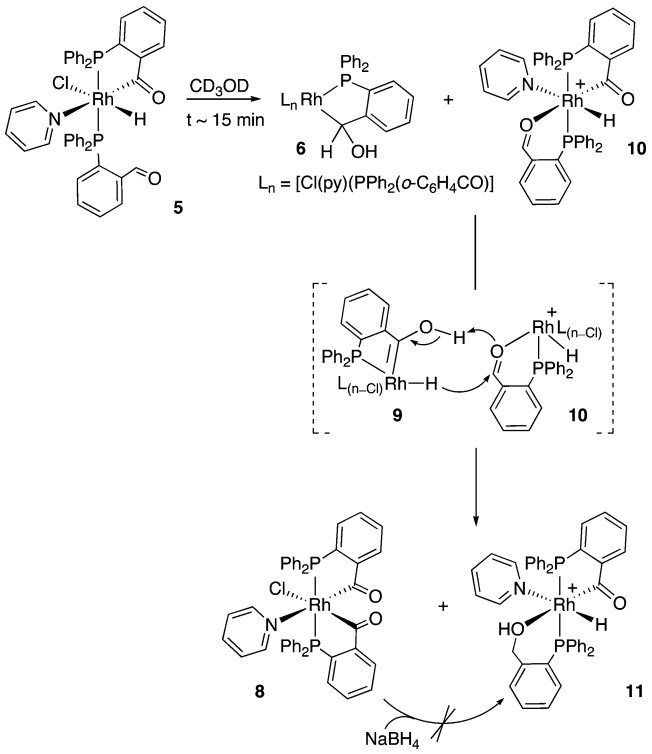


the J(P,P) coupling constant of 336 Hz agrees with a trans arrangement of the phosphorus atoms. The chemical shift of the hydride, −14.25 ppm, indicates it being trans to the nitrogen atom of the pyridine ligand.

If longer reaction periods are allowed, up to 2 h, complex **5** reacts in methanol to give a mixture of the diacyl derivative **8**, the acyl hydrido alcohol species **11**, and a small amount of the acyl hydrido aldehyde complex **10**. Complex **8** could be separated by filtration with a maximum yield of ca. 40% with respect to the starting rhodium material. The remaining solution contained complex **11** that was always contaminated with at least 10% of **10**. Attempts to obtain **11** as the main product by performing the reaction with bubbling of hydrogen gas proved unsuccessful and led to the same product distribution as that obtained in the absence of H_2.

By following the reaction of **5** in CD_3OD by NMR, we have observed at 253 K the initial formation of the cationic complex **10**. When the temperature is raised up to 293 K, a mixture

Scheme 5



containing almost equimolar amounts of complexes **10**, **6**, and **11** is observed along with the appearance of a precipitate that corresponds to the diacyl derivative **8** (see Scheme 5). Most likely, dissociation of the aldehyde group in the initially formed **10** allows partial formation of **6**. After 2 h the resonances due to complexes **6** and **10** decrease while the amount of **11** in the solution and also the amount of precipitated **8** increases markedly. No incorporation of deuterium in the hydrogenated aldehyde is observed, thus excluding a mechanism involving H-transfer from methanol to aldehyde. The resonances due to the methylene group of the hydrogenated complex **11** appear as two sharp doublets, at 4.83 and 4.30 ppm (J_{gem} = 12.8 Hz), respectively. The coupling with the hydroxy proton is lost, due to its exchange with the deuterated solvent.

These observations point to a bimolecular bifunctional ionic mechanism as being responsible for the hydrogenation of the cationic phosphine−aldehyde complex **10** to give the phosphine−alcohol derivative **11**, with the hydroxyalkyl complex **6** being the source of both proton and hydride, as shown in Scheme 5. The transient hydrido hydroxycarbene **9**, formed from **6** by α-hydrogen transfer, contains a hydride and a hydroxy group that can interact with the O-coordinated C═O bond in complex **10**. The experimental evidence for this mechanism can be summarized as follows. (i) The coordinated aldehyde in **10** requires the presence of proton and hydride to undergo the hydrogenation. It reacts with a hydride source, borohydride, in a protic solvent, methanol, but fails to react with H_2. (ii) In the absence of $NaBH_4$, the reaction products **8** and **11** are always contaminated with the aldehyde derivative **10** because the intermediate **9** can lose H_2 (see Scheme 3), thus preventing the complete reduction of the aldehyde. (iii) In a separate experiment we have observed that complex **8** fails to react with $NaBH_4$ in methanol, and therefore **8** is not a source for **11** under these reaction conditions. This mechanism is similar to the hydrogenation process reported by Casey et al. for the catalytic hydrogenation of ketones and aldehydes with ruthenium hydrides containing OH groups.[38] The hydrogenation of polar bonds involving outer-sphere mechanisms do not require coordination of the substrate to the transition metal.[8] In the present case an outer-sphere mechanism appears to be involved but O-coordination of the aldehyde to the rhodium atom of another molecule is required to effectively undergo hydrogenation.

Conclusions

This report has demonstrated that rhodium acyl hydrido complexes containing N-donor ligands show some acidic character of the Rh−H bond and are able to form acyl hydroxyalkyl derivatives by their reaction with aldehydes. In protic solvents, where the formation of rhodium acyl hydrido aldehyde complexes is also possible, hydrogenation to the rhodium acyl hydrido alcohol complexes can occur. According to the experimental observations, a bimolecular bifunctional ionic mechanism, involving formation of a transient hydrido hydroxycarbene as a source of proton and hydride and interacting with a coordinated aldehyde, appears feasible. The same transient species can explain the dehydrogenation of the acyl hydroxyalkyl species to afford a diacyl derivative.

Experimental Section

General Procedures. The preparation of the metal complexes was carried out at room temperature under nitrogen by standard Schlenk techniques. $[RhCl(COD)]_2$[39] and complex **7**[14b] were prepared as previously reported. Microanalysis were carried out with a Leco CHNS-932 microanalyser. Conductivities were measured in acetone solution with a Metrohm 712 conductimeter. IR spectra were recorded with a Nicolet FTIR 510 spectrophotometer in the range 4000−400 cm^{-1} using KBr pellets. NMR spectra were recorded with a Bruker Avance DPX 300 or Bruker Avance 500 spectrometer; ^1H and $^{13}C\{^1H\}$ (TMS internal standard), $^{31}P\{^1H\}$ (H_3PO_4 external standard), and 2D spectra were measured from $CDCl_3$, C_6D_6, toluene-d_8, or CD_3OD solution. Mass spectra were recorded on a VG Autospec instrument, by liquid secondary ion (LSI) MS using nitrobenzyl alcohol as matrix and a cesium gun (Universidad de Zaragoza).

Warning! Perchlorate salts and transition-metal perchlorate complexes may be explosive. Preparations on a scale larger than that reported herein should be avoided.

[RhHCl(PPh$_2$(*o*-C$_6$H$_4$CO))(py)$_2$] (1). To a benzene solution of $[RhCl(COD)]_2$ (30 mg, 0.06 mmol) was added pyridine (19 mg, 0.24 mmol), whereupon a yellow solid was formed. Addition of PPh_2(*o*-C_6H_4CHO) (35 mg, 0.12 mmol) and stirring for 2 h gave a yellow solid that was filtered off, washed with benzene, and vacuum-dried. Yield: 76%. IR (KBr, cm^{-1}): 2061 (m), ν(RhH); 1620 (s), ν(C═O). ^1H NMR ($CDCl_3$): δ −15.93 (dd, 1H, J(Rh,H) = 23.8 Hz, J(P,H) = 18.3 Hz, Rh*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 78.2 (d, J(Rh,P) = 165 Hz). Anal. Calcd for $C_{29}H_{25}ClN_2OPRh$: C, 59.35; H, 4.29; N, 4.77. Found: C, 59.01; H, 4.62; N, 4.66.

[RhCl$_2$(PPh$_2$(*o*-C$_6$H$_4$CO))(py)$_2$] (2). A chloroform solution of $[RhHCl(PPh_2(o\text{-}C_6H_4CO))(py)_2]$ (**1**; 46 mg, 0.078 mmol) was stirred for 24 h. Addition of methanol to the solution gave a yellow solid that was filtered off, washed with methanol, and vacuum-dried. Yield: 13%. IR (KBr, cm^{-1}): 1649 (s), ν(C═O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 59.4 (d, J(Rh,P) = 134 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 229.2 (dd, J(Rh,C) = 28 Hz, J(P,C) = 3 Hz, Rh*C*O). FAB MS (*m*/*z*): calcd for $C_{29}H_{24}Cl_2N_2OPRh$, 620; observed, 585 $[M - Cl]^+$.

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Anal. Calcd for $C_{29}H_{24}Cl_2N_2OPRh \cdot 0.75CHCl_3$: C, 50.27; H, 3.51; N, 3.94. Found: C, 49.98; H, 3.70; N, 3.97.

[$RhCl_2(PPh_2(o\text{-}C_6H_4CO))(bdh)$] (3). To a dichloromethane solution of [$RhCl_2(PPh_2(o\text{-}C_6H_4CO))(py)_2$] (**2**; 31 mg, 0.05 mmol) was added biacetyl dihydrazone (9 mg, 0.075 mmol). Stirring for 2 h followed by addition of diethyl ether gave a yellow solid that was filtered off, washed with diethyl ether, and vacuum-dried. Yield: 46%. IR (KBr, cm^{-1}): 3386 (s), 3340 (s), 3295 (s), $\nu(NH_2)$; 1655(s), $\nu(C{=}O)$. ^1H NMR ($CDCl_3$): δ 2.50 (s, 3H, CH_3); 2.19 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.1 (d, J(Rh,P) = 134 Hz). Anal. Calcd for $C_{23}H_{24}Cl_2N_4OPRh$: C, 47.86; H, 4.19; N, 9.71. Found: C, 48.03; H, 4.36; N, 10.39.

[$RhHCl(PPh_2(o\text{-}C_6H_4CO))(PPh_3)(py)$] (4). To a dichloromethane solution of **1** (46 mg, 0.078 mmol) was added triphenylphosphine (21 mg, 0.078 mmol). Stirring for 1 h followed by addition of diethyl ether gave a yellow solid that was filtered off, washed with diethyl ether, and vacuum-dried. Yield: 42%. IR (KBr, cm^{-1}): 2044 (m), ν(RhH); 1623 (s), $\nu(C{=}O)$. ^1H NMR ($CDCl_3$): δ −14.55 (ddd, 1H, J(Rh,H) = 18.3 Hz, $J(PPh_3,H)$ = 11.9 Hz, $J(PPh_2(o\text{-}C_6H_4CO),H)$ = 4.6 Hz, Rh*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.72 (dd, J(Rh,P) = 140 Hz, J(P,P) = 375 Hz, $PPh_2(o\text{-}C_6H_4CO)$); 42.7 (dd, J(Rh,P) = 124 Hz, PPh_3). Anal. Calcd for $C_{42}H_{35}ClNOP_2Rh$: C, 65.51; H, 4.58; N, 1.82. Found: C, 64.98; H, 4.65; N, 1.87.

Formation and Characterization of [$RhHCl(PPh_2(o\text{-}C_6H_4CO))(\kappa^1\text{-}PPh_2(o\text{-}C_6H_4CHO))(py)$] (5). To a toluene-$d_8$ solution of [$RhCl(COD)]_2$ (15 mg, 0.03 mmol) at 253 K was added pyridine (10 mg, 0.12 mmol), whereupon a yellow solid was formed. Addition of $PPh_2(o\text{-}C_6H_4CHO)$ (35 mg, 0.12 mmol) led to a solution for which the NMR spectra were obtained at 253 K. Data for **5** are as follows. ^1H NMR (toluene-d_8): δ 10.72 (s, 1H, $PPh_2(o\text{-}C_6H_4CHO)$); −13.85 (m, 1H, Rh*H*). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 67.9 (dd, J(Rh,P) = 139 Hz, J(P,P) = 370 Hz, $PPh_2(o\text{-}C_6H_4CO)$); 42.9 (dd, J(Rh,P) = 123 Hz, $PPh_2(o\text{-}C_6H_4CHO)$).

[$RhCl(PPh_2(o\text{-}C_6H_4CO))(PPh_2(o\text{-}C_6H_4CHOH))(py)$] (6). Method a. To a benzene suspension of [$RhHCl(PPh_2(o\text{-}C_6H_4CO))(\kappa^2\text{-}PPh_2(o\text{-}C_6H_4CHO))$] (**7**; 43 mg, 0.06 mmol) was added pyridine (5 mg, 0.06 mmol), whereupon dissolution of the solid occurred. After the mixture was stirred for 4 h, the solvent was evaporated and the solid residue was dissolved in dichloromethane. Addition of diethyl ether gave a yellow solid that was filtered off, washed with diethyl ether, and vacuum-dried. Yield: 62%.

Method b. To a benzene solution of [$RhCl(COD)]_2$ (30 mg, 0.06 mmol) was added pyridine (10 mg, 0.12 mmol), whereupon a yellow solid was formed. Addition of $PPh_2(o\text{-}C_6H_4CHO)$ (70 mg, 0.24 mmol) and stirring for 90 min gave a cloudy solution that was filtered. The solvent was evaporated, and the solid residue was dissolved in dichloromethane. Addition of diethyl ether gave a yellow solid that was filtered off, washed with diethyl ether, and vacuum-dried. Yield: 22%. The solid obtained was suspended in methanol, stirred for 5 min, filtered off, washed with methanol, and vacuum-dried to obtain an analytically pure sample (yield 35%). IR (KBr, cm^{-1}): 3564 (m, br), ν(OH); 1614 (s), $\nu(C{=}O)$. Anal. Calcd for $C_{43}H_{35}ClNO_2P_2Rh.0.75CH_3OH$: C, 63.92; H, 4.66; N, 1.70. Found: C, 63.94; H, 4.56; N, 1.75. Data for **6a** are as follows. ^1H NMR ($CDCl_3$): δ 8.48 (s, 1H, $PPh_2(o\text{-}C_6H_4CHOH)$); 6.75 (from HSQC correlation, $PPh_2(o\text{-}C_6H_4CHOH)$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 54.1 (dd, J(Rh,P) = 155 Hz, J(P,P) = 19 Hz, $PPh_2(o\text{-}C_6H_4CHOH)$); 30.9 (dd, J(Rh,P) = 85 Hz, $PPh_2(o\text{-}C_6H_4CO)$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 243.7 (dd, J(Rh,C) = 34 Hz, J(P,C) = 8 Hz, Rh*C*O); 93.1 (dd, J(Rh,C) = 22 Hz, J(P,C) = 100 Hz, Rh*C*HOH). Data for **6b** are as follows. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 53.3 (dd, J(Rh,P) = 160 Hz, J(P,P) = 20 Hz, $PPh_2(o\text{-}C_6H_4CHOH)$); 33.6 (dd, J(Rh,P) = 88 Hz, $PPh_2(o\text{-}C_6H_4CO)$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 234.8 (m, Rh*C*O); 96.4 (dd, J(Rh,C) = 22 Hz, J(P,C) = 96 Hz, Rh*C*HOH).

[$RhCl(PPh_2(o\text{-}C_6H_4CO))_2(py)$] (8). To a methanol suspension of [$RhCl(COD)]_2$ (30 mg, 0.06 mmol) was added pyridine (19 mg, 0.24 mmol), whereupon a yellow solid was formed. Adding $PPh_2(o\text{-}C_6H_4CHO)$ (70 mg, 0.24 mmol) and stirring overnight gave a yellow solid that was filtered off, washed with methanol, and vacuum-dried. Yield: 36%. IR (KBr, cm^{-1}): 1637 (s), $\nu(C{=}O)$. $^{31}P\{^1H\}$ NMR (253 K, $CDCl_3$): δ 61.8 (dd, J(Rh,P) = 152 Hz, J(P,P) = 336 Hz, P_A); 51.6 (dd, J(Rh,P) = 138 Hz, P_B). $^{13}C\{^1H\}$ NMR (253 K, $CDCl_3$): δ 234.2 (d, J(Rh,C) = 36 Hz, Rh*C*O); 232.8 (d, J(Rh,C) = 33 Hz, Rh*C*O). Anal. Calcd for $C_{43}H_{33}ClNO_2P_2Rh \cdot CH_3OH$: C, 63.82; H, 4.50; N, 1.69. Found: C, 63.46; H, 4.16; N, 1.95.

[$RhH(PPh_2(o\text{-}C_6H_4CO))(\kappa^2\text{-}PPh_2(o\text{-}C_6H_4CHO))(py)$]$BPh_4$ ([10]-BPh_4). To a benzene solution of [$RhCl(COD)]_2$ (30 mg, 0.06 mmol) was added pyridine (19 mg, 0.24 mmol), whereupon a yellow solid was formed. Addition of $PPh_2(o\text{-}C_6H_4CHO)$ (70 mg, 0.24 mmol) led to a solution. Evaporation of the solvent, dissolution of the solid residue in methanol, and addition of $NaBPh_4$ (41 mg, 0.12 mmol) led to a yellow solid that was filtered off, washed with methanol, and vacuum-dried. Yield: 80%. IR (KBr, cm^{-1}): 2032 (m), ν(RhH); 1655 (s), 1635 (s), $\nu(C{=}O)$. Λ_M (Ω^{-1} cm^2 mol^{-1}): 63 (acetone). ^1H NMR ($CDCl_3$): δ −13.88 (ddd, 1H, J(RhH) = 20.6 Hz, $J(PPh_2(o\text{-}C_6H_4CHO),H)$ = 14.1 Hz, $J(PPh_2(o\text{-}C_6H_4CO),H)$ = 6.0 Hz, Rh*H*); 8.61 (s, C*H*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 59.4 (dd, J(Rh,P) = 134 Hz, J(P,P) = 346 Hz, $PPh_2(o\text{-}C_6H_4CO)$); 32.1 (dd, J(Rh,P) = 128 Hz, $PPh_2(o\text{-}C_6H_4CHO)$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 228.4 (d, J(Rh,C) = 34 Hz, Rh*C*O); 201.3 (s, *C*HO). FAB MS (*m*/*z*): calcd for $C_{43}H_{35}NO_2P_2Rh$, 762; observed, 762 $[M]^+$. Anal. Calcd for $BC_{67}H_{55}NO_2P_2Rh \cdot CH_3OH$: C, 73.32; H, 5.34; N, 1.26. Found: C, 73.18; H, 5.16; N, 1.43.

[$RhH(PPh_2(o\text{-}C_6H_4CO))(\kappa^2\text{-}PPh_2(o\text{-}C_6H_4CH_2OH))(py)$]$ClO_4$ ([11]ClO_4). To a benzene solution of [$RhCl(COD)]_2$ (30 mg, 0.06 mmol) was added pyridine (19 mg, 0.24 mmol), whereupon a yellow solid was formed. Addition of $PPh_2(o\text{-}C_6H_4CHO)$ (70 mg, 0.24 mmol) led to a solution. The solvent was evaporated, and the solid residue was dissolved in methanol. Addition of $NaBH_4$ (5 mg, 0.12 mmol) and $NaClO_4$ (15 mg, 0.12 mmol) with vigorous stirring gave a yellow solid that was filtered off, washed with methanol, and vacuum-dried. Yield: 65%. IR (KBr, cm^{-1}): 3432 (m, br), ν(OH); 2035 (w), ν(RhH); 1634 (s), $\nu(C{=}O)$. Λ_M (Ω^{-1} cm^2 mol^{-1}): 114 (acetone). ^1H NMR ($CDCl_3$): δ −14.25 (ddd, 1H, J(RhH) = 20.1 Hz, $J(PPh_2(o\text{-}C_6H_4CH_2OH),H)$ = 13.2 Hz, $J(PPh_2(o\text{-}C_6H_4CO),H)$ = 5.5 Hz, Rh*H*); 5.12 (dd, 1H, J_{gem} = 12.8 Hz, J(H,H) = 4.6 Hz, CH_2); 4.44 (dd, 1H, J(H,H) = 5.5 Hz, CH_2); 6.19 (pseudotriplet, 1H, O*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 62.3 (dd, J(Rh,P) = 136 Hz, J(P,P) = 336 Hz, $PPh_2(o\text{-}C_6H_4CO)$; 29.3 (dd, J(Rh,P) = 126 Hz, $PPh_2(o\text{-}C_6H_4CH_2OH)$. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 230.1 (d, J(Rh,C) = 32 Hz, Rh*C*O); 67.6 (d, J(P,C) = 7 Hz, *C*H_2OH). FAB MS (*m*/*z*): calcd for $C_{43}H_{37}NO_2P_2Rh$, 764; observed, 764 $[M]^+$. Anal. Calcd for $C_{43}H_{37}ClNO_6P_2Rh$: C, 59.77; H, 4.32; N, 1.62. Found: C, 59.25; H, 4.52; N, 1.66.

Reaction of [$RhHCl(PPh_2(o\text{-}C_6H_4CO))(\kappa^1\text{-}PPh_2(o\text{-}C_6H_4CHO))(py)$] (5) in Methanol. To a benzene solution of [$RhCl(COD)]_2$ (50 mg, 0.10 mmol) was added pyridine (32 mg, 0.40 mmol), whereupon a yellow solid was formed. Addition of $PPh_2(o\text{-}C_6H_4CHO)$ (118 mg, 0.40 mmol) led to a solution of **5**. The solvent was evaporated, the solid residue was dissolved in methanol, and stirring for 2 h gave a yellow precipitate that was filtered, washed with methanol, and vacuum-dried. This solid was identified spectroscopically as complex **8** (yield 40% with respect to the rhodium starting material). The remaining solution was taken to dryness. According to the NMR spectra, the solid residue contained complex **11** with a 10% impurity of **10**, on the basis of the integration of the hydride resonances of both compounds.

X-ray Structure Determination of 8. Yellow prismatic single crystals of complex **8**, suitable for X-ray diffraction, were successfully grown from a solution of 9 mg of complex **6** in 1 mL of methanol at room temperature. Data collection was carried out at room temperature on a Bruker Smart CCD diffractometer using

Table 2. Crystal and Refinement Data for [RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(py)]·MeOH (8)

empirical formula	$[C_{43}H_{33}ClNO_2P_2Rh]\cdot CH_3OH$
formula wt	828.05
temp (K)	293(2)
wavelength (Å)	0.71073
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	
a (Å)	9.2621(6)
b (Å)	10.6197(7)
c (Å)	20.613(1)
α (deg)	89.520(1)
β (deg)	86.157(1)
γ (deg)	69.962(1)
V (Å^3)	1900.3(2)
Z	2
calcd density (g cm^{-3})	1.447
abs coeff (mm^{-1})	0.646
F(000)	848
cryst size (mm^3)	0.22 × 0.13 × 0.09
θ range for data collecn (deg)	0.99−25.00
index ranges	$-10 \le h \le 11$, $-12 \le k \le 12$, $-19 \le l \le 24$
no. of rflns collected	9983
no. of indep rflns	6603 (R(int) = 0.0341)
completeness to $\theta = 25.00°$ (%)	98.8
no. of data/restraints/params	6603/1/229
goodness of fit on F^2	1.019
final R^a indices ($I > 2\sigma(I)$)	0.0417 (4671 obsd rflns)
$R_w{}^b$ indices (all data)	0.1113
largest diff peak and hole (e Å^{-3})	0.510 and −0.902

[a] $\sum[|F_o| - |F_c|]/\sum|F_o|$. [b] $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) operating at 50 kV and 20 mA. The data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each exposure of 10 s covered 0.3° in ω. The first 100 frames were re-collected at the end of the data collection to monitor crystal decay after X-ray exposition, and no appreciable drop in the intensities was observed. A summary of the fundamental crystal data is given in Table 2. The structure was solved by direct methods and conventional Fourier techniques. The refinement was made by full-matrix least squares on F^2 (SHELX-97).[40] Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms, with some exceptions. After the last cycles of refinement the Fourier difference map showed electronic density; this was assigned to one solvent molecule of CH_3OH. The carbon and oxygen atoms were refined in three isotropical cycles, and in subsequent cycles their thermal parameters were kept constant while their coordinates were refined with geometric restraints and a variable common C−O distance. All hydrogen atoms were calculated at geometrical positions and refined as riding on their respective carbon atoms. These features led to R and R_w factors of 0.0414 (4671 reflections observed) and 0.1127 (all reflections), respectively. The largest residual peak in the final difference map is 0.503 e Å^{-3}.

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Supporting Information Available: A CIF file giving crystallographic data for complex **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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