Selective Formation of Rhodium Diacyl or Acyl Hydrido Hemiaminal Complexes in the Reaction of *o*-(Diphenylphosphino)benzaldehyde with Rhodium 2-Aminopyridine or 2-(Aminomethyl)pyridine Compounds

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[RhCl(COD)]$_2$ (COD = 1,5-cyclooctadiene) reacts with PPh$_2$(*o*-C$_6$H$_4$CHO) in the presence of 2-aminopyridine (apy) to give the diacyl [RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(apy)] (**1**) with evolution of hydrogen. **1** is a mixture of two isomers, **1a** with trans P atoms and cis acyl groups and **1b** with cis P atoms and trans acyl groups. In solution fast exchange between phosphorus atoms of the two isomers and also decreasing of the **1a**:**1b** ratio occur on raising the temperature. This behavior can be due to intramolecular opening of the acyl-phosphine chelate. Complex **1** reacts with bidentate N-donor ligands to afford cationic diacyl derivatives [Rh(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(NN)]$^+$ (NN = 2,2′-bipyridine, **2**; glyoxaldihydrazone, **3**; 1,2-phenylenediamine, **4**; ethylenediamine, **5**; 2-(aminomethyl)pyridine (ampy), **6**, **7**; 8-aminoquinoline (aqui), **8**) with high stereoselectivity depending on the N-donor ligand employed. Diimine ligands give only complexes with trans phosphorus atoms (**2**, **3**), diamine ligands give only derivatives containing cis phosphorus atoms (**4**, **5**), and ligands containing amino-imine functionalities afford both types of isomers. Ampy allows the isolation of both complexes **6** and **7**. Complex **6**, with trans phosphorus atoms, is the kinetic product of the reaction, and **7**, with cis phosphorus atoms, is the most stable thermodynamic isomer. The rate of the isomerization reaction of **6** into **7** depends on the solvent and also on the counterion, suggesting that this reaction may be assisted by ion-pair formation via hydrogen bonding. The reaction of [RhCl(COD)]$_2$ with PPh$_2$(*o*-C$_6$H$_4$CHO) in the presence of ampy or the reaction of the phosphine-aldehyde complex [RhClH(PPh$_2$(*o*-C$_6$H$_4$CO))(κ^2-PPh$_2$(*o*-C$_6$H$_4$CHO))] (**10**) with ampy leads to [RhH(PPh$_2$(*o*-C$_6$H$_4$CO))(PNN)]Cl (**9**) (PNN = κ^3-PPh$_2$(*o*-C$_6$H$_4$CHOH-NH-CH$_2$-C$_5$H$_4$N)), containing a hemiaminal group (>CH(OH)NH−) formed by the reaction of the aldehyde with the amino group. Complex **10** reacts with aqui to afford [RhH(PPh$_2$(*o*-C$_6$H$_4$CO))(PPh$_2$(*o*-C$_6$H$_4$CH=N-C$_9$H$_6$N))]$^+$ (**11**), containing a PNN ligand with an imine functionality. The hemiaminal stability seems to be favored by the presence of a single sp^3 carbon atom in **9**. All the complexes were fully characterized spectroscopically. Single-crystal X-ray diffraction analysis was performed on **1a** and **7**.

Introduction

The C−H bond cleavage in aldehydes, promoted by transition metal complexes, is an active area of research.[1] Rhodium and iridium compounds oxidatively add aldehyde C−H bonds to afford acyl hydride derivatives,[2] and this type of species is believed to be involved in catalytic processes such as aldehyde decarbonylation or alkene hydroacylation.[3] Recently we have reported that *o*-(diphenylphosphino)benzaldehyde reacts with rhodium(I) complexes in the presence of pyridine to afford the coordination of two phosphines and the oxidative addition of only one aldehyde to give an acyl hydrido derivative containing an uncoordinated aldehyde, [RhHCl(PPh$_2$(*o*-C$_6$H$_4$CO))(κ^1-PPh$_2$-(*o*-C$_6$H$_4$CHO))(py)], which transforms readily into an acyl hydroxyalkyl derivative, [RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))(PPh$_2$(*o*-C$_6$H$_4$-CHOH))(py)], by migration of hydride to the aldehyde. The acyl hydroxyalkyl derivative may lose H$_2$ to give the corresponding diacyl complex [RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(py)], which contains trans phosphorus atoms.[4] We thought it would be interesting to study the reaction of *o*-(diphenylphosphino)-

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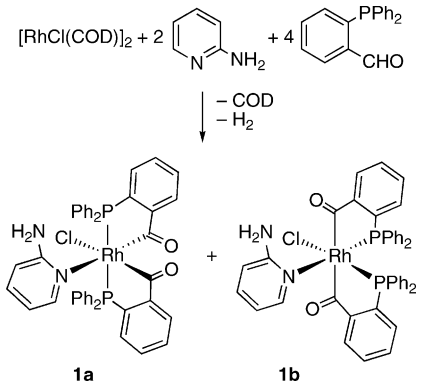
benzaldehyde with rhodium complexes in the presence of aminopyridines such as 2-aminopyridine or 2-(aminomethyl)-pyridine. The presence of the amino group can influence the course of the reactions observed in the presence of pyridine and can also lead to the formation of a new carbon−nitrogen bond by its reaction with aldehyde. 2-Aminopyridine forms a variety of complexes behaving as a monodentate *N*-pyridine ligand.[5] Usually, simple chelate complexes are unstable because of ring strain, and a bridging mode between two metal centers is favored.[6] Whenever an electron-rich element is available, the formation of conventional N−H---X hydrogen bonds is frequent.[7] In Ir(III) hydrido complexes also containing phosphines, 2-aminopyridine has been found to form intramolecular hydrogen bonds such as N−H---X−Ir (X = F, Cl, Br, I) and also N−H---H−Ir interactions, and for these complexes the H---H hydrogen bond has been reported to be stronger than the H---Cl hydrogen bond.[8] Recently 2-aminopyridine has also been found to establish a weak N−H---Pt hydrogen-bonding interaction in Pt(II) complexes.[9] It is known that 2-aminopyridine may react with Fisher-type carbenes to afford chelating aminocarbenes.[10] The reaction of acyl hydroxycarbene platinum(II) complexes with this ligand has been recently reported to yield cyclic aminocarbene derivatives.[11] 2-Aminopyridine rhodium-(I) complexes have been found to be effective catalysts for the homogeneous hydrogenation of olefins[12] and a catalytic system of rhodium(I) and 2-aminopicoline is useful in olefin or alkyne hydroacylation and in carbon−carbon bond activation among others.[13] The 2-(aminomethyl)pyridine ligand, containing a methylene spacer group between the pyridyl and the amino nitrogen donor sites, has been less thoroughly studied. It behaves usually as a bidentate chelating ligand[5b,14,15] and may also afford polymeric complexes with the ampy ligand bridging adjacent units.[16] 2-(Aminomethyl)pyridine phosphine ruthenium(II) complexes are active catalysts in ketone hydrogenation and specially active when transfer hydrogenation is used.[15] Recently a 2-(aminomethylpyridine) ruthenium(II) complex has been reported to behave as a highly selective protein kinase inhibitor.[17]

Scheme 1



We report now on the reactions of rhodium compounds with $PPh_2(o\text{-}C_6H_4CHO)$ in the presence of 2-aminopyridine or 2-(aminomethyl)pyridine and establish the influence of the amino or aminomethyl group on the high selectivity of the observed reactions. Dehydrogenation, formation of diacyl diphosphine derivatives with cis or trans phosphine groups, and formation of new C−N bonds with stabilization of intermediates of the aldehyde imination reactions, depending on the N-donor ligand, are described.

Results and Discussion

Diacyl Formation. The reaction of $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) with $PPh_2(o\text{-}C_6H_4CHO)$ in the presence of 2-aminopyridine (apy) leads to the diacyl derivative $[RhCl(PPh_2(o\text{-}C_6H_4CO))_2(apy)]$ (**1**) as a mixture of **1a** with trans P atoms and cis acyl groups and **1b** with cis P atoms and trans acyl groups, with displacement of COD and evolution of hydrogen, as shown in Scheme 1. This reaction probably follows a reaction sequence similar to that recently reported in the presence of pyridine[4] instead of 2-aminopyridine, but in the present case the presence of the amino group in the apy ligand promotes a faster reaction sequence and also allows the formation of complexes with cis P atoms such as **1b**, unobserved when pyridine was used in this reaction. Complex **1** contains a noncoordinated amino group. Previously the reaction between an amino group and one aldehyde has been reported to afford new carbon−nitrogen bonds in five- or seven-member chelated metallocycles.[18] Apy is suitable for Schiff base formation,[19] though it now appears that in the present system the formation of a new carbon−nitrogen bond to give a four- or an eight-membered chelated metallocycle is not favored.

The IR spectrum of **1** shows three absorptions for the amino group at lower wavenumbers than the free ligand, suggesting

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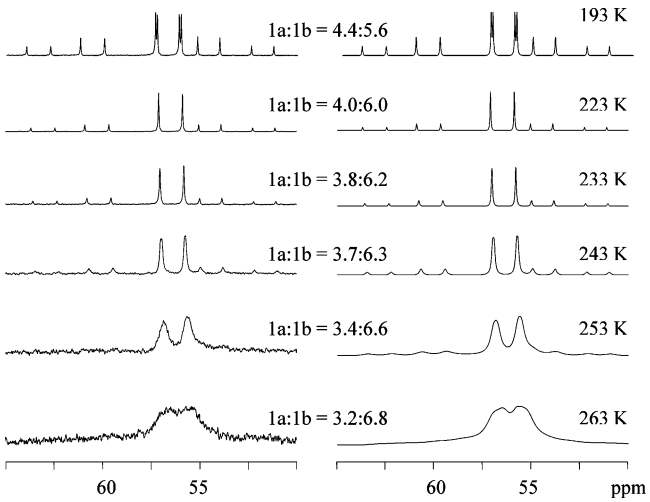

Figure 1. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **1** in CD_2Cl_2: (left) experimental and (right) calculated.

the formation of hydrogen bonding.[20] At 193 K the $^{31}P\{^1H\}$ NMR spectrum (see Figure 1) contains an ABX spin pattern (X = ^{103}Rh) along with two close doublets, indicating the presence in solution of a mixture of two isomers **1a** and **1b** in a 4.4:5.6 ratio, calculated by line-shape analysis.[21] Complex **1a**, with trans phosphorus atoms and cis acyl groups, is responsible for the ABX spin system (J(P,P) = 337 Hz). Complex **1b** contains two cis phosphorus atoms, giving rise to only two doublets due to unobservable J(P,P). The J(Rh,P) coupling constants of ca. 140 Hz are consistent with phosphorus atoms with trans to low trans effect ligands such as pyridine or chloride[22] and indicate the presence of two mutually trans acyl groups. The $^{13}C\{^1H\}$ NMR spectrum contains four doublets in the 230−240 ppm region, due to rhodium-bonded acyl groups cis to phosphorus atoms, and the ^1H NMR spectrum contains two singlets due to the amino groups at 8.19 and 4.26 ppm, which disappear upon addition of a few drops of CD_3OD. The resonance at 8.19 ppm, at lower field than in the free ligand by more than 3 ppm, suggests the existence of hydrogen bonding also in solution.[8a]

Complex **1** is fluxional in solution, as shown by inspection of the $^{31}P\{^1H\}$ NMR spectra obtained from CD_2Cl_2 solutions in the 193−303 K range (see Figure 1). When the temperature is raised, the amount of **1a** decreases smoothly while that of **1b** increases, reaching a **1a**:**1b** = 4.0:6.0 ratio at 223 K. At higher temperatures broadening of the resonances is also observed due to fast exchange between phosphorus atoms of the two isomers. At 263 K, the **1a**:**1b** ratio is 3.2:6.8 and the coalescence is attained. From line-shape analysis of the variable-temperature $^{31}P\{^1H\}$ NMR spectra in the 223−263 K range,[21] the activation parameters $\Delta H^{\ddagger} = 14.0 \pm 0.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = 7.4 \pm 1$ cal K^{-1} mol^{-1} have been determined. The relatively small value of the entropy of activation falls in the range between 11 and −10 cal K^{-1} mol^{-1}, reported to be indicative of intramolecular rearrangement processes.[23] We believe that opening of the acyl-phosphine chelate can account for the observed fluxional behavior and allows the isomerization reaction. Attempts to obtain calculated spectra using line-shape analysis that fit the experimental data at temperatures higher than 263 K proved unsuccessful. Another process, yet unidentified, is responsible for the fluxional behavior at temperatures higher than 263 K. These results show that the isomer ratio depends on the temperature. Isomer **1a** contains the phosphines mutually trans and the best σ-donor acyl groups trans to the more electronegative atoms nitrogen and chloride. Its stability increases at lower temperatures, as expected when the electronic effects are taken into consideration,[24] but at higher temperatures the amount of **1b** increases.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1a and [7]ClO_4 Including the Hydrogen Bond Geometry[a]

1a		[**7**]ClO_4	
Rh1−C20	2.015(5)	Rh1−C20	2.051(9)
Rh1−C1	1.998(5)	Rh1−C1	1.991(9)
Rh1−P1	2.345(2)	Rh1−P1	2.434(2)
Rh1−P2	2.355(2)	Rh1−P2	2.272(2)
Rh1−N1	2.305(4)	Rh1−N1	2.120(7)
Rh1−Cl1	2.576(1)	Rh1−N2	2.213(7)
C1−O1	1.220(6)	C1−O1	1.223(9)
C20−O2	1.205(6)	C20−O2	1.222(9)
N1−C39	1.357(7)		
N1−C43	1.348(7)		
N2−C43	1.337(8)		
C20−Rh1−C1	88.2(2)	C20−Rh1−C1	88.6(3)
C20−Rh1−N1	93.7(2)	C20−Rh1−N1	88.6(3)
C20−Rh1−Cl1	168.7(2)	C20−Rh1−N2	87.5(3)
C20−Rh1−P1	92.7(2)	C20−Rh1−P1	171.7(2)
C20−Rh1−P2	80.8(2)	C20−Rh1−P2	80.4(3)
N1−Rh1−P1	94.5(1)	N1−Rh1−P1	88.7(2)
N1−Rh1−P2	90.9(1)	N1−Rh1−P2	168.9(2)
C1−Rh1−P2	90.2(2)	C1−Rh1−P2	89.5(2)
C1−Rh1−N1	177.9(2)	C1−Rh1−N1	91.3(3)
C1−Rh1−Cl1	80.5(2)	C1−Rh1−N2	169.4(3)
P1−Rh1−P2	171.8(1)	P1−Rh1−P2	102.4(1)
Hydrogen Bond			
N2−H2A	0.92	N2−H2A	0.98
H2A---Cl1	2.43	H2A---O4	2.17
N2---Cl1	3.164(5)	N2---O4	3.02(1)
N2−H2A−Cl1	136.5	N2−H2A−O4	145.0
N2−H2B	1.01	N2−H2B	0.97
H2B---Cl1′	2.64	H2B---O2″	2.57
N2---Cl1′	3.506(5)	N2---O2″	3.33(1)
N2−H2B−Cl1′	144.0	N2−H2B−O2″	135.1

[a] (′) $-x+2, -y+1, -z+1$; (″) $-x+1, -y+1, -z+2$.

Only **1a** formed X-ray quality crystals upon layering dichloromethane solutions of **1** with diethyl ether. The X-ray diffraction study confirms the structure depicted in Scheme 1. Selected bond distances and angles are listed in Table 1, and Figure 2 shows a molecular drawing. The geometry about the metal atom is distorted octahedral, both phosphorus atoms are mutually trans, the acyl groups are mutually cis, and the distances comprising the chelate ligands are in the expected ranges.[4,18,25] As previously observed,[9,26] the N−C distances involved in the C−N−C−NH_2 fragment of apy are equal within the experimental error owing to delocalization of the π-electron density including the amino group. A strong intramolecular hydrogen bond, N2−H2A−Cl, is formed between the amino group and the chlorine atom. A weaker intermolecular hydrogen bond, N2−H2B−Cl1′, between the amino group of one molecule and the chlorine atom of a centrosymmetric one leads to the formation of a dimer.

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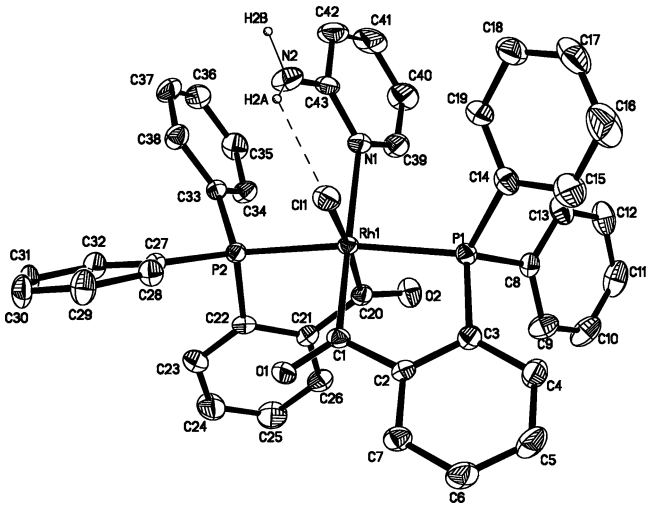
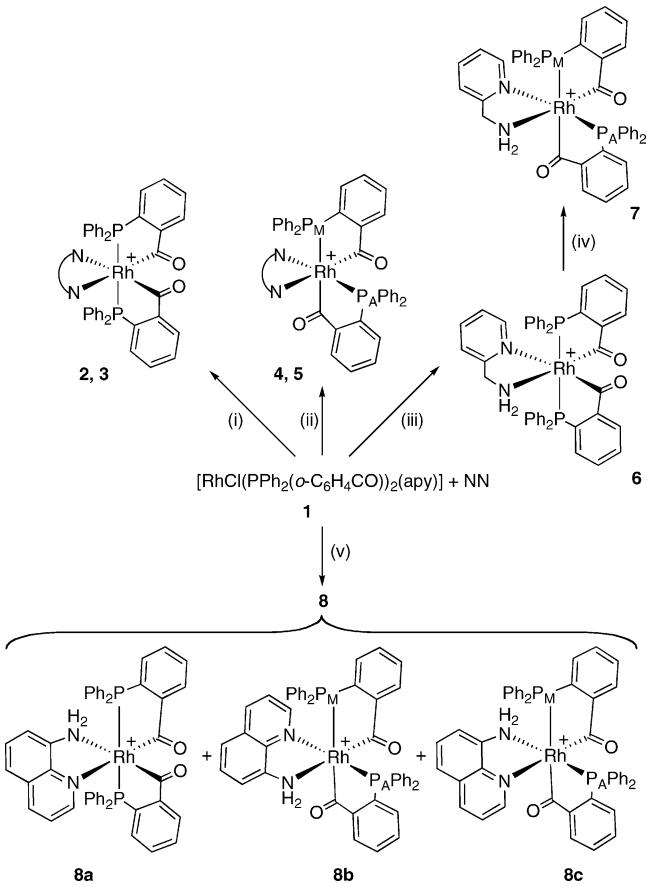


Figure 2. ORTEP view of complex **1a** showing the atomic numbering and the intramolecular hydrogen bonds (25% probability ellipsoids). The hydrogen atoms except two have been omitted for clarity.

Cationic Diacyl Complexes. To confirm the influence of the amino group in promoting the formation of diacyl diphosphine complexes with cis phosphorus atoms, we studied the reactions of **1** with different bidentate N-donors. The reactions proceed with displacement of the pyridinic ligand and also of chloride and afford cationic diacyl derivatives $[Rh(PPh_2(o\text{-}C_6H_4CO))_2(NN)]^+$ (NN = 2,2′-bipyridine (bipy), **2**; glyoxaldihydrazone (gdh), **3**; 1,2-phenylenediamine (daphen), **4**; ethylenediamine (en), **5**; 2-(aminomethyl)pyridine (ampy), **6**, **7**; 8-aminoquinoline (aqui), **8**). The corresponding complexes have been isolated as tetraphenylborate or perchlorate compounds by addition of the corresponding sodium salts (see Experimental Section). As shown in Scheme 2, the stereochemistry of the obtained complexes depends markedly on the N-donor ligand employed, so that diimine ligands lead only to complexes with trans phosphorus atoms, diamine ligands give only derivatives containing cis phosphorus atoms, and ligands containing amino-imine functionalities afford both types of isomers. A high selectivity is observed in this reaction. The obtained complexes show the expected features in their IR spectra, their FAB spectra show the parent peaks, and they behave as 1:1 electrolytes in acetone solution.[27]

When aromatic (bipy) or aliphatic (gdh) diimines are employed, complex **2** or **3** shown in Scheme 2i is formed, respectively. Their $^{31}P\{^1H\}$ NMR spectra show only one doublet at 53 ppm with a J(Rh,P) of 137 Hz, which agrees with trans P atoms. The $^{13}C\{^1H\}$ NMR spectra show only one doublet at 235 ppm with a J(Rh,C) of 32 Hz, corresponding to equivalent acyl groups. By using aromatic (daphen) or aliphatic (en) diamine ligands, the reaction gives complex **4** or **5**, respectively (see Scheme 2ii), which could be fully characterized by spectroscopic means. The $^{31}P\{^1H\}$ NMR spectra contain two doublets of doublets, consistent with an AMX pattern due to two mutually cis phosphorus atoms (J(P,P) of 20 Hz). The resonances that appear around 64 ppm agree with phosphorus atoms trans to nitrogen (J(Rh,P) $\approx$ 155 Hz), while the resonances at 30 ppm are consistent with phosphorus atoms trans to the acyl groups (J(Rh,P) $\approx$ 80 Hz). Accordingly, the $^{13}C\{^1H\}$ NMR spectra show two doublets of doublets, at ca. 240 and 230 ppm, respectively. The resonances at lower field are due to acyl groups trans to phosphorus (J(P,C) $\approx$ 110 Hz), while the resonances at higher field correspond to the acyl groups trans to nitrogen.

Scheme 2 [a]



[a] (i) NN = bipy, **2**; gdh, **3**; in CH_2Cl_2. (ii) NN = daphen, **4**, in CH_2Cl_2; en, **5**, in MeOH. (iii) NN = ampy; 15 min at 298 K in MeOH; 15 min at 253 K in $CDCl_3$. (iv) 20 h at 298 K in MeOH; 2 h at 298 K in CH_2Cl_2. (v) NN = aqui, in CH_2Cl_2.

In accordance with these results the amino-imine ligands ampy and aqui allow the formation of complexes with trans phosphorus atoms and also of complexes with cis phosphorus atoms. By using the ampy ligand, containing an aliphatic amino group and an aromatic imine, both complexes could be obtained pure. In methanol solution the fast formation of the trans derivative **6** occurs as shown in Scheme 2iii, and the addition of sodium tetraphenylborate allows the isolation of the corresponding [**6**]BPh_4. A longer reaction time (ca. 20 h) in methanol solution leads to the formation of the cis derivative **7** (see Scheme 2iv). These results suggest that complex **6**, with trans phosphorus atoms, is the kinetic product of the reaction in methanol solution, while complex **7**, with cis phosphorus atoms, is the most stable thermodynamic isomer. The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of [**6**]BPh_4, [**7**]ClO_4, and [**7**]BPh_4 confirm the stereochemistry of **6** and **7**. Recently, a related isomerization reaction has been observed for $Ru(H)_2(PPh_3)_2$(ampy), containing hydrides instead of acyl groups, but in the Ru(II) derivative the most stable product contains mutually trans phosphorus atoms and nitrogen atoms trans to hydrides.[15]

The rate of the isomerization reaction of **6** into **7** depends markedly on the solvent and also on the counterion. When the reaction of **1** with ampy is performed in dichloromethane solution at room temperature, the fast formation of **7** is accomplished. By following this reaction by NMR in $CDCl_3$ solution at 253 K the immediate formation of [**6**]Cl is observed, which on warming to 293 K transforms into [**7**]Cl. The

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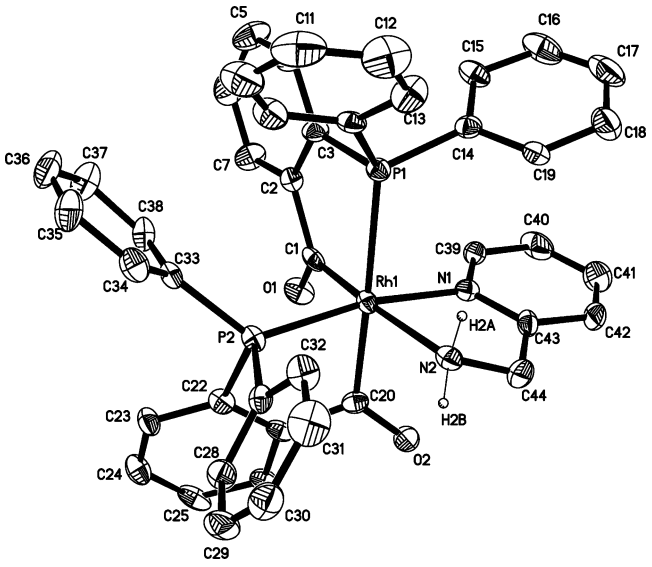

Figure 3. ORTEP view of complex **7** showing the atomic numbering (25% probability ellipsoids). The hydrogen atoms except two and the labeling of some C atoms have been omitted for clarity.

appearance of a broad resonance at 4.48 ppm due to the amino groups and displaced by ca. 2.7 ppm from that of free ampy (1.74 ppm) suggests some extent of hydrogen bonding in solution.[8a] In $CDCl_3$ solution the isomerization of [**6**]BPh_4 into [**7**]BPh_4 also occurs but at a much lower rate so that after 2 months a [**6**]BPh_4:[**7**]BPh_4 = 1.7:8.3 ratio is attained. The amino protons for [**6**]BPh_4 and [**7**]BPh_4 are observed at 1.98 and 1.10 or 1.23 and 1.10 ppm, respectively, close to those of free ampy.

We thus observe that the higher the ability of the counterion and the lower the ability of the solvent to form hydrogen bonds, the higher the reaction rate of the isomerization reaction. These observations suggest that this reaction may be assisted by ion-pair formation via hydrogen bonding. In chlorinated solvents ion pairing, available for X = Cl and not available for X = BPh_4, makes the reaction faster when X = Cl. In solvents with higher dielectric constants such as methanol, efficient ion solvation may prevent ion pairing and make the isomerization reaction slower than in dichloromethane. The role of the counterion and of the solvent in the course of many stoichiometric and catalytic processes involving transition metal complexes has long been recognized.[28]

On only spectroscopic grounds it is not possible to determine which N-donor group, pyridine or amine, is trans to the phosphorus atom in complex **7**; therefore an X-ray diffraction study was undertaken on [**7**]ClO_4. The crystal structure consists of discrete *cis*-[Rh(PPh_2(*o*-C_6H_4CO))$_2$(ampy)] cations and ClO_4^- anions held together by hydrogen bonding. The cation shows a distorted octahedral geometry. Selected bond distances and angles, including the hydrogen bond, are listed in Table 1, and Figure 3 shows an ORTEP view of the cation. The P1−Rh1−P2 angle (102.4 (1)°) confirms that the phosphorus atoms are mutually cis. The C1−Rh1−N2 and the N1−Rh1−P2 angles (169.4(3)° and 168.9(2)°) indicate that the amino group is trans to acyl and the pyridinic nitrogen is trans to phosphorus, respectively. This disposition with the amino ligand trans to the group with higher trans influence has also been proposed for a related Ru(H)$_2$(PPh_3)$_2$(ampy) complex.[15] The Rh−N, Rh−P, and Rh−C distances are in the expected ranges,[18,25] and the corresponding values for each type of bond differ significantly. The Rh1−P1 distance with P1 trans to acyl is 0.16(1) Å longer that the Rh1−P2 distance with P2 trans to the iminic nitrogen, the Rh1−C20 distance with C20 trans to phosphorus is 0.06(1) Å longer than the Rh1−C1 distance with Cl trans to the aminic nitrogen, and the Rh1−N2 distance with N2 trans to acyl is 0.09(1) Å longer than the Rh1−N1 distance, with N1 trans to phosphorus. These differences agree with the trans influence order of the ligands: acyl ≫ phosphine > amine ≥ pyridine.[29] A hydrogen bond N2−H2A---O4 is observed between the coordinated amino group and an oxygen atom of the perchlorate anion (N2---O4 = 3.02(1) Å). The amino group forms another hydrogen bond, N2−H2B---O2″, weaker, with the oxygen atom of an acyl group in a neighboring cation (N2---O2″ = 3.33(1) Å). This intermolecular interaction leads to the formation of dimers.

The aqui ligand, containing both aromatic amino and imino groups, gives a mixture of isomers with the phosphorus atoms mutually trans or mutually cis, which we were unable to separate. It has been previously observed that this ligand favors the formation of isomer mixtures when forming acyl hydrido rhodium derivatives.[18a] The NMR study at room temperature in $CDCl_3$ solution indicates that [Rh(PPh_2(*o*-C_6H_4CO))$_2$(aqui)]-BPh_4 (**8**) consists of a mixture of three isomers, shown in Scheme 2v, in the ratio **8a**:**8b**:**8c** = 4.2:4.2:1.6. Complex **8a** contains trans phosphorus atoms, while **8b** and **8c** contain phosphorus atoms mutually cis (see Experimental Section). Because in complex **7** the amino group is trans to the acyl group, we propose that **8b**, with the amino group trans to the acyl group, is the major cis isomer in compound **8**, though the reverse assignment cannot be excluded.

Hemiaminal Formation. The reaction of [RhCl(COD)]$_2$ with PPh_2(*o*-C_6H_4CHO) in the presence of ampy leads to the formation of an ionic acyl hydrido derivative, *trans*-[RhH(PPh_2-(*o*-C_6H_4CO))(Pampy)]Cl (**9a**), containing a terdentate PNN ligand (Pampy = PPh_2(*o*-C_6H_4CHOH-NH-CH_2-C_5H_4N)), though unpure. Complex **9a** can be obtained pure by the reaction of ampy with an acyl hydrido complex containing a phosphine-aldehyde chelating ligand, [RhClH(PPh_2(*o*-C_6H_4CO))(κ^2-PPh_2-(*o*-C_6H_4CHO))] (**10**),[18c] as shown in Scheme 3. Chloride displacement occurs and the terdentate Pampy ligand in **9a** is formed by the reaction of the aldehyde functionality with the amino group. In this case the imination reaction does not go to completion but gives the intermediate hemiaminal group (>CH-(OH)NH−) N-coordinated to the rhodium atom.

Complex **9a** behaves as an electrolyte in acetone solution though the molar conductivity is below the usual range for 1:1 electrolytes,[27] most likely due to ion pairing. Its infrared spectrum contains the expected absorptions at 3425 and 3144 cm^{-1} due respectively to the OH and to the coordinated NH groups. The NMR data, including 2D experiments, confirm the formation of the hemiaminal group and the structure shown in Scheme 3. The $^{13}C\{^1H\}$ NMR spectrum shows the resonance due to the >CH(OH)NH− group at 81.7 ppm as a doublet, most likely due to coupling with rhodium (J(Rh,C) = 14 Hz). This signal correlates in the HSQC experiment with a singlet at 6.50 ppm. In the ^1H NMR spectrum of **9a** the signals due to NH

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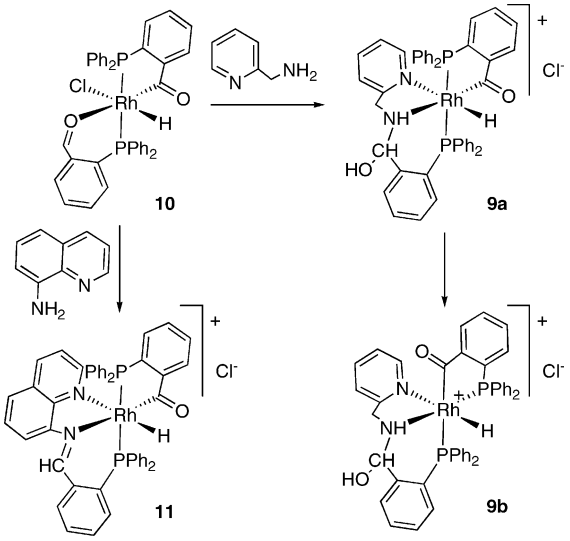
Scheme 3



(6.09 ppm) and OH (1.74 ppm) appear as singlets and agree with other reported data,[18b,30] and the hydride resonance (−13.52 {qt} ppm) indicates it being trans to nitrogen. The $^{31}P\{^1H\}$ NMR spectrum corresponds to two phosphorus atoms mutually trans (J(P,P) = 331 Hz), and the resonance of the new terdentate ligand PNN in a six-membered metallocycle appears at higher field (34.1 ppm) than the resonance of the acyl-phosphine chelate forming a five-membered metallocycle (62.4 ppm), as expected.[31] All these data indicate the presence of only one isomer in solution. As in other complexes containing PNN terdentate ligands formed by the reaction of aldehyde with amines,[18] we believe that in **9a** the hydride is most likely trans to the unreacted pyridine group.

The isolation of **9a** was unexpected. When complex **10** reacts with the amino-imine ligand aqui, the imination reaction of the aldehyde goes to completion to afford the complex *trans*-[RhH(PPh$_2$(*o*-C$_6$H$_4$CO))(PPh$_2$(*o*-C$_6$H$_4$CH═N−C$_9$H$_6$N))]$^+$, **11**, as shown in Scheme 3. Complex **11** has been previously obtained by the reaction of [RhCl(COD)]$_2$ with PPh$_2$(*o*-C$_6$H$_4$CHO) in the presence of the amino-imine ligand aqui.[18a] The condensation reaction in hemiaminals to afford the corresponding imines by hydrogen transfer from N to O is usually very easy and needs both H and OH to be on the same side of the N−C bond.[32] Because of this requirement, some stable hemiaminals in cyclic molecules are known,[33] and previously we have reported on rhodium complexes [RhH(PPh$_2$(*o*-C$_6$H$_4$CO))(PPh$_2$(*o*-C$_6$H$_4$-CHOH-NH-N═C(R)C(R)═NNH$_2$))]$^+$ containing noncoordinated stable hemiaminals in seven-membered rings of terdentate PNN ligands, formed from diimino-coordinated dihydrazones.[18] We observe now that this intermediate can also be stabilized when N-coordinated to rhodium in a six-membered PN metallocycle.

Both species **9** and **11** contain terdentate PNN ligands forming a six-membered RhNCCCP and a five-membered RhNCCN metallocycle, and with the N atom involved in the formation of the new carbon−nitrogen bond bonded to the rhodium atom. It appears now that the hemiaminal stability in **9** is favored by the presence of a sp^3 and a sp^2 carbon atom in the five-membered metallocycle. In **11**, and in other related complexes,[18a] the carbon atoms in the RhNCCN metallocycle are sp^2. Also, diethylenetriamine, containing two sp^3 carbon atom spacers between the N atoms, reacts with PPh$_2$(*o*-C$_6$H$_4$CHO) in the presence of palladium or silver complexes to afford the imination products with six-membered MNCCCP metallocycles containing the imine functionalities and five-membered MNCCN metallocycles.[34]

As previously discussed for *trans*-[Rh(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(ampy)]$^+$ (**6**), complex **9a**, containing two mutually trans phosphorus atoms, isomerizes to *cis*-[RhH(PPh$_2$(*o*-C$_6$H$_4$CO))(Pampy)]Cl (**9b**), containing two mutually cis phosphorus atoms, in CDCl$_3$ solution. Unfortunately, decomposition of both complexes occurs in solution before the transformation of **9a** into **9b** is completed, thus preventing the isolation of **9b**. The NMR spectra of mixtures of both complexes confirm the cis disposition of the phosphorus atoms in **9b** (J(P,P) = 12 Hz) and the hydride being trans to nitrogen (−15.57 {dt} ppm). The presence of the hemiaminal group is also confirmed by the $^{13}C\{^1H\}$ NMR spectrum, which shows a doublet at 82.6 ppm due to coupling with rhodium (J(Rh,C) = 16 Hz). Other spectroscopic data for **9b** are as expected (see Experimental Section).

Conclusions

Chelate-assisted aldehyde dehydrogenation by rhodium complexes to afford diacyl derivatives is favored by the presence of the nonchelating 2-aminopyridine. In the presence of the chelating 2-(aminomethyl)pyridine the reaction between the amino group and the aldehyde is preferred, and the combination of sp^3 and sp^2 carbon spacers in the N-donor ligand allows the isolation of the intermediate hemiaminal product. Cationic cis-diacyl trans-diphosphine or cis-diacyl cis-diphosphine complexes can be selectively prepared by selecting the appropriate N-donor ligands. The amino groups favor the cis-diphosphine disposition and the isomerization reactions appear to be assisted by ion-pair formation via hydrogen bonding.

Experimental Section

General Procedures. The preparation of the metal complexes was carried out at room temperature under nitrogen by standard Schlenk techniques. [RhCl(COD)]$_2$[35] and complex **10**[18c] were prepared as previously reported. Microanalyses were carried out with a Leco CHNS-932 microanalyzer. 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 Bruker Avance DPX 300 or Bruker Avance 500 spectrometers, ^1H and $^{13}C\{^1H\}$ (TMS internal standard), $^{31}P\{^1H\}$ (H_3PO_4 external standard), and 2D spectra were measured from $CDCl_3$, DMSO-d_6, or CD_2Cl_2 solutions. Mass spectra were recorded on a VG Autospec, by liquid secondary ion (LSI) MS using nitrobenzyl alcohol as matrix and a cesium gun (Universidad de Zaragoza).

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

[RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(apy)] (1). To a dichloromethane solution of [RhCl(COD)]$_2$ (30 mg, 0.06 mmol) was added 2-aminopyridine (11.3 mg, 0.12 mmol), whereupon a yellow solid was formed. Addition of PPh$_2$(*o*-C$_6$H$_4$CHO) (70 mg, 0.24 mmol) and

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stirring during 2 h gave a yellow solid, which was filtered off, washed with dichloromethane, and vacuum-dried. Yield: 58%. IR (KBr, cm^{-1}): 3393(s), 3277(s), 3176(s), $\nu(NH_2)$; 1630(s), $\nu(C{=}O)$. Data for **1a**. ^1H NMR (193 K, CD_2Cl_2): δ 6.06 (d, 1H, $J(H,H) = 8.6$ Hz, H^3); 5.73 (t, 1H, $J(H,H) = 6.8$ Hz, H^5). $^{31}P\{^1H\}$ NMR (193 K, CD_2Cl_2): δ 61.8 (dd, $J(Rh,P) = 150$ Hz, $J(P,P) = 337$ Hz, P_A); 53.4 (dd, $J(Rh,P) = 138$ Hz, P_B). $^{13}C\{^1H\}$ NMR (193 K, CD_2Cl_2): δ 239.4 (d, $J(Rh,C) = 35$ Hz, Rh*C*O); 231.2 (d, $J(Rh,C) = 30$ Hz, Rh*C*O). Data for **1b**. ^1H NMR (193 K, CD_2Cl_2): δ 5.84 (d, 1H, $J(H,H) = 8.6$ Hz, H^3); 6.15 (t, 1H, $J(H,H) = 6.8$ Hz, H^5). $^{31}P\{^1H\}$ NMR (193 K, CD_2Cl_2): δ 56.8 (d, $J(Rh,P) = 147$ Hz); 56.6 (d, $J(Rh,P) = 148$ Hz). $^{13}C\{^1H\}$ NMR (193 K, CD_2Cl_2): δ 230.0 (d, $J(Rh,C) = 37$ Hz, Rh*C*O); 229.0 (d, $J(Rh,C) = 32$ Hz, Rh*C*O). Anal. Calcd for $C_{43}H_{34}ClN_2O_2P_2Rh{\cdot}0.25CH_2Cl_2$: C, 62.42; H, 4.18; N, 3.37. Found: C, 62.32; H, 4.56; N, 3.52.

***trans*-[Rh(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(NN)]BPh$_4$ (NN = bipy, 2; gdh, 3).** To a dichloromethane suspension of [RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(apy)] (**1**) (40.5 mg, 0.05 mmol) was added 2,2′-bipyridine (7.8 mg, 0.05 mmol) or glyoxaldihydrazone (4.3 mg, 0.05 mmol). Stirring for 90 min followed by addition of $NaBPh_4$ (17.1 mg, 0.05 mmol) in methanol gave a yellow solid, which was filtered off, washed with methanol, and vacuum-dried. Data for **2**: Yellow. Yield: 72%. IR (KBr, cm^{-1}): 1641(s), $\nu(C{=}O)$. Λ_M (ohm^{-1} cm^2 mol^{-1}): 89 (acetone). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 52.4 (d, $J(Rh,P) = 138$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 235.5 (d, $J(Rh,C) = 32$ Hz, Rh*C*O). FAB-MS: calcd for $C_{48}H_{36}N_2O_2P_2Rh$, 837; obsd, 837 $[M]^+$. Anal. Calcd for $C_{72}H_{56}BN_2O_2P_2Rh{\cdot}0.75CH_2Cl_2$: C, 71.59; H, 4.75; N, 2.30. Found: C, 71.35; H, 4.84; N, 2.47. Data for **3**: Pale pink. Yield: 76%. IR (KBr, cm^{-1}): 3408(s), 3278(s), $\nu(NH_2)$; 1649(s), $\nu(C{=}O)$. Λ_M (ohm^{-1} cm^2 mol^{-1}): 69 (acetone). ^1H NMR ($CDCl_3$): δ 5.18 (s, 2H, *H*C═N); 4.97 (s, 4H, N*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 53.2 (d, $J(Rh,P) = 136$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 236.0 (d, $J(Rh,C) = 32$ Hz, Rh*C*O). Anal. Calcd for $C_{64}H_{54}BN_4O_2P_2Rh{\cdot}0.25CH_2Cl_2$: C, 69.65; H, 4.96; N, 5.06. Found: C, 69.61; H, 4.77; N, 5.39.

***cis*-[Rh(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(NN)]BPh$_4$ (NN = daphen, 4; en, 5).** To a dichloromethane or methanol suspension of [RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(apy)] (**1**) (40.5 mg, 0.05 mmol) was added 1,2-phenylenediamine (5.4 mg, 0.05 mmol) or ethylenediamine (3.0 mg, 0.05 mmol), respectively. Stirring for 90 or 15 min followed by addition of $NaBPh_4$ (17.1 mg, 0.05 mmol) in methanol gave a yellow solid, which was filtered off, washed with methanol, and vacuum-dried. Data for **4**: Yield: 78%. IR (KBr, cm^{-1}): 3296(m), 3218(m), $\nu(NH_2)$; 1644(s), $\nu(C{=}O)$. Λ_M (ohm^{-1} cm^2 mol^{-1}): 87 (acetone). ^1H NMR (DMSO-d_6): δ 6.27 (d, 1H, $J_{gem} = 12.8$ Hz, N*H*); 6.10 (d, 1H, $J_{gem} = 11.9$ Hz, N*H*); 5.93 (s, 1H, N*H*); 5.74 (d, 1H, $J_{gem} = 12.8$ Hz, N*H*). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 64.7 (dd, $J(Rh,P) = 156$ Hz, $J(P,P) = 19$ Hz, P_A); 31.2 (dd, $J(Rh,P) = 82$ Hz, P_M). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 240.9 (dd, $J(Rh,C) = 29$ Hz, $J(P,C) = 113$ Hz, RhC_AO); 231.0 (dd, $J(Rh,C) = 28$ Hz, $J(P,C) = 10$ Hz, RhC_MO). FAB-MS: calcd for $C_{44}H_{36}N_2O_2P_2Rh$, 789; obsd, 789 $[M]^+$. Anal. Calcd for $C_{68}H_{56}BN_2O_2P_2Rh{\cdot}0.25CH_2Cl_2$: C, 72.54; H, 5.04; N, 2.48. Found: C, 72.48; H, 5.23; N, 2.68. Data for **5**. Yield: 60%. IR (KBr, cm^{-1}): 3315(m), 3263(m), $\nu(NH_2)$; 1644(s), $\nu(C{=}O)$. Λ_M (ohm^{-1} cm^2 mol^{-1}): 87 (acetone). ^1H NMR ($CDCl_3$): δ 3.78 (s, 2H, N*H*); 2.28 (s, 1H, C*H*); 2.22 (s, 2H, N*H*); 1.44 (s, 1H, C*H*); 1.08 (s, 1H, C*H*); 0.52 (s, 1H, C*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.1 (dd, $J(Rh,P) = 154$ Hz, $J(P,P) = 20$ Hz, P_A); 30.5 (dd, $J(Rh,P) = 79$ Hz, P_M). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 239.2 (dd, $J(Rh,C) = 30$ Hz, $J(P,C) = 108$ Hz, RhC_AO); 233.9 (dd, $J(Rh,C) = 29$ Hz, $J(P,C) = 9$ Hz, RhC_MO); 41.7 (s, CH_2); 44.9 (s, CH_2). Anal. Calcd for $C_{64}H_{56}BN_2O_2P_2Rh{\cdot}$MeOH: C, 71.44; H, 5.53; N, 2.56. Found: C, 71.06; H, 5.30; N, 2.64.

***trans*-[Rh(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(ampy)]BPh$_4$ ([6]BPh$_4$).** To a methanol suspension of [RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(apy)] (**1**) (40.5 mg, 0.05 mmol) was added 2-aminomethyl)pyridine (5.3 mg, 0.05 mmol). Stirring for 15 min followed by addition of $NaBPh_4$ (17.1 mg, 0.05 mmol) gave a yellow solid, which was filtered off, washed with methanol, and vacuum-dried. Yield: 83%. IR (KBr, cm^{-1}): 3319(m), 3278(m), $\nu(NH_2)$; 1620(s), $\nu(C{=}O)$. Λ_M (ohm^{-1} cm^2 mol^{-1}): 84 (acetone). ^1H NMR ($CDCl_3$): δ 2.36 (m, 1H, C*H*); 2.18 (m, 1H, C*H*); 1.98 (s, 1H, N*H*); 1.10 (s, 1H, N*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 56.3 (dd, $J(Rh,P) = 141$ Hz, $J(P,P) = 303$ Hz, P_A); 54.1 (dd, $J(Rh,P) = 140$ Hz, P_B). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 232.4 (d, $J(Rh,C) = 31$ Hz, Rh*C*O); 235.7 (d, $J(Rh,C) = 30$ Hz, Rh*C*O); 48.1 (s, CH_2). FAB-MS: calcd for $C_{44}H_{36}N_2O_2P_2Rh$, 789; obsd, 789 $[M]^+$. Anal. Calcd for $C_{68}H_{56}BN_2O_2P_2Rh{\cdot}0.5$MeOH: C, 73.14; H, 5.20; N, 2.49. Found: C, 72.93; H, 5.02; N, 2.82.

***cis*-[Rh(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(ampy)]A (A = ClO$_4$, ([7]ClO$_4$); A = BPh$_4$, ([7]BPh$_4$)). Method a.** To a methanol suspension of [RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(apy)] (**1**) (40.5 mg, 0.05 mmol) was added 2-(aminomethyl)pyridine (5.3 mg, 0.05 mmol). Stirring for 20 h followed by addition of $NaClO_4$ (7.0 mg, 0.05 mmol) gave a yellow solid, which was filtered off, washed with methanol, and vacuum-dried. Yield: 40%.

Method b. To a dichloromethane suspension of [RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(apy)] (**1**) (40.5 mg, 0.05 mmol) was added 2-(aminomethyl)pyridine (5.3 mg, 0.05 mmol). Stirring for 2 h followed by addition of $NaBPh_4$ (17.1 mg, 0.05 mmol) in methanol solution and evaporation of dichloromethane gave a yellow solid, which was filtered off, washed with methanol, and vacuum-dried. Yield: 55%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.3 (dd, $J(Rh,P) = 154$ Hz, $J(P,P) = 18$ Hz, P_A); 27.5 (dd, $J(Rh,P) = 77$ Hz, P_M). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 236.4 (dd, $J(Rh,C) = 30$ Hz, $J(P,C) = 110$ Hz, RhC_AO); 236.6 (dd, $J(Rh,C) = 30$ Hz, $J(P,C) = 9$ Hz, RhC_MO); 50.2 (s, CH_2). Data for [**7**]ClO$_4$. Λ_M (ohm^{-1} cm^2 mol^{-1}): 122 (acetone). IR (KBr, cm^{-1}): 3334(m), 3288(m), $\nu(NH_2)$; 1641(s), 1622(s) $\nu(C{=}O)$. ^1H NMR ($CDCl_3$): δ 4.34 (s, 2H, C*H*); 4.09 (s, 1H, N*H*); 1.86 (s, 1H, N*H*). Anal. Calcd for $C_{44}H_{36}ClN_2O_6P_2Rh{\cdot}2CH_3OH$: C, 57.97; H, 4.65; N, 2.94. Found: C, 57.11; H, 4.05; N, 3.21. Data for [**7**]BPh$_4$. Λ_M (ohm^{-1} cm^2 mol^{-1}): 82 (acetone). IR (KBr, cm^{-1}): 3339(m), 3267(m), $\nu(NH_2)$; 1648(s), 1625(s), $\nu(C{-}O)$. ^1H NMR ($CDCl_3$): δ 2.57 (m, 1H, C*H*); 2.37 (m, 1H, C*H*); 1.23 (s, 1H, N*H*); 1.10 (s, 1H, N*H*). Anal. Calcd for $C_{68}H_{56}BN_2O_2P_2Rh{\cdot}0.75CH_2Cl_2$: C, 70.42; H, 4.94; N, 2.39. Found: C, 69.84; H, 5.06; N, 2.69.

[Rh(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(aqui)]BPh$_4$ (8). To a dichloromethane suspension of [RhCl(PPh$_2$(*o*-C$_6$H$_4$CO))$_2$(apy)] (**1**) (40.5 mg, 0.05 mmol) was added 8-aminoquinoline (7.2 mg, 0.05 mmol). Stirring for 90 min followed by addition of $NaBPh_4$ (17.1 mg, 0.05 mmol) in methanol solution gave a yellow solid, which was filtered off, washed with methanol, and vacuum-dried. Yield: 65%. IR (KBr, cm^{-1}): 3304(m), 3252(m), $\nu(NH_2)$; 1646(s), $\nu(C{=}O)$. Λ_M (ohm^{-1} cm^2 mol^{-1}): 77 (acetone). Data for **8a**. ^1H NMR ($CDCl_3$): δ 3.92 (d, 1H, J_{gem}= 13.7 Hz, N*H*); 2.90 (d, 1H, N*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 58.6 (dd, $J(Rh,P) = 143$ Hz, $J(P,P) = 300$ Hz, P_A); 53.3 (dd, $J(Rh,P) = 139$ Hz, P_B). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 233.5 (d, $J(Rh,C) = 33$ Hz, Rh*C*O); 232.8 (d, $J(Rh,C) = 32$ Hz, Rh*C*O). Data for **8b**. ^1H NMR ($CDCl_3$): δ 6.89 (from COSY correlation, N*H*); 5.12 (d, 1H, J_{gem}= 7.3 Hz, N*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.3 (dd, $J(Rh,P) = 159$ Hz, $J(P,P) = 19$ Hz, P_A); 29.8 (dd, $J(Rh,P) = 76$ Hz, P_M). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 232.7 (dd, $J(Rh,C) = 30$ Hz, $J(P,C) = 110$ Hz, RhC_AO); 234.2 (dd, $J(Rh,C) = 30$ Hz, $J(P,C) = 10$ Hz, RhC_MO). Data for **8c**. ^1H NMR ($CDCl_3$): δ 3.34 (d, 1H, J_{gem}= 12.8 Hz, N*H*); 3.04 (d, 1H, N*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 64.2 (dd, $J(Rh,P) = 164$ Hz, $J(P,P) = 21$ Hz, P_A); 27.5 (dd, $J(Rh,P) = 80$ Hz, P_M). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 238.0 (dd, $J(Rh,C) = 29$ Hz, $J(P,C) = 109$ Hz, RhC_AO); 229.1 (dd, $J(Rh,C) = 28$ Hz, $J(P,C) = 10$ Hz, RhC_MO). Anal. Calcd for $C_{71}H_{56}BN_2O_2P_2Rh{\cdot}0.25CH_2Cl_2$: C, 73.39; H, 4.88; N, 2.40. Found: C, 72.92; H, 4.85; N, 2.62.

[RhH(PPh$_2$(*o*-C$_6$H$_4$CO))(Pampy)]Cl (9). To a benzene suspension of [RhHCl(PPh$_2$(*o*-C$_6$H$_4$CO))(κ^2-PPh$_2$(*o*-C$_6$H$_4$CHO))] (50.3 mg,

Table 2. Crystal Data and Structure Refinement for Compounds 1a and [7]ClO_4

	1a	[**7**]ClO_4
empirical formula	$[C_{43}H_{34}ClN_2O_2P_2Rh]\cdot Et_2O$	$[C_{44}H_{36}N_2O_2P_2Rh]ClO_4\cdot 1/2Et_2O$
fw	885.14	926.11
wavelength (Å)	0.71073	0.71073
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.778(1)	9.671(1)
b (Å)	13.098(1)	12.964(2)
c (Å)	15.503(1)	18.056(2)
α (deg)	79.172(2)	99.173(2)
β (deg)	80.900(2)	90.822(3)
γ (deg)	79.961(2)	109.949(2)
volume (Å^3)	2098.7(3)	2095.0(5)
Z	2	2
density (calcd) (Mg/m^3)	1.401	1.468
absorp coeff (mm^{-1})	0.590	0.601
F(000)	912	950
θ range (deg)	1.35 to 25.0	1.70 to 25.0
index ranges	−12, −12, −18 to 12, 15, 17	−11, −14, −20 to 11, 15, 21
no. of reflns collected	10 976	16 124
no. of indep reflns	7280 [R(int) = 0.0515]	7189 [R(int) = 0.1215]
completeness to θ (deg)	98.3%	97.1%
no. of data/restraints/params	7280/5/475	7189/0/519
R^a [$I > 2\sigma(I)$]	0.0549(5194 obsd reflns)	0.061 (3080 obsd reflns)
$R_{wF}{}^b$ (all data)	0.1564	0.1594

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

0.07 mmol) was added 2-aminomethylpyridine (14.8 mg, 0.14 mmol). Stirring for 90 min gave a pale yellow solid, which was filtered off, washed with benzene, and vacuum-dried. Yield: 58%. IR (KBr, cm^{-1}): 3425(s), ν(OH); 3144(s), ν(NH); 2033(m), ν(RhH); 1642(s), ν(C═O). Λ_M (ohm^{-1} cm^2 mol^{-1}): 39 (acetone). Data for **9a**. ^{1}H NMR ($CDCl_3$): δ −13.52 (qt, 1H, J(Rh,H) = 20.6 Hz, J(P,H) = 15.4; 5.1 Hz, Rh*H*); 6.50 (from HSQC, C*H*OH); 6.09 (s, br, 1H, N*H*); 4.25 (d, 1H, J_{gem}= 18.0 Hz, C*H*); 3.19 (dd, 1H, J(H,H) = 6.8 Hz, C*H*); 1.74 (s, 1H, CHO*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 62.4 (dd, J(Rh,P) = 134 Hz, J(P,P) = 331 Hz, *P*Ph_2-(*o*-C_6H_4CO)); 34.1 (dd, J(Rh,P) = 122 Hz, *P*ampy). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 228.2 (m, Rh*C*O); 81.7 (d, J(Rh,C) = 14 Hz, *C*HOH); 49.1 (s, *C*H_2). FAB-MS: calcd for $C_{44}H_{38}N_2O_2P_2Rh$, 791; obsd, 791 [M]$^+$. Anal. Calcd for $C_{44}H_{38}ClN_2O_2P_2Rh$: C, 63.90; H, 4.63; N, 3.39. Found: C, 63.27; H, 4.61; N, 3.31. Data for **9b**. ^{1}H NMR ($CDCl_3$): δ −15.57 (dt, 1H, J(Rh,H) = 21.4 Hz, J(P,H) = 21.4; 9.2 Hz, Rh*H*); 5.47 (d, 1H, J_{gem}= 15.3 Hz, C*H*); 4.61 (dd, 1H, J(H,H) = 6.1 Hz, C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 71.2 (dd, J(Rh,P) = 148 Hz, J(P,P) = 12 Hz, *P*Ph_2(*o*-C_6H_4CO)); 13.7 (dd, J(Rh,P) = 71 Hz, *P*ampy). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 82.6 (d, J(Rh,C) = 16 Hz, *C*HOH); 50.6 (s, *C*H_2).

X-ray Structure Determination of 1a and [7]ClO_4. Yellow prismatic single crystals of $[C_{43}H_{34}ClN_2O_3P_2Rh]\cdot Et_2O$ (**1a**) and needles of $[C_{44}H_{36}N_2O_2P_2Rh]ClO_4\cdot 1/2Et_2O$ [**7**]ClO_4 suitable for X-ray diffraction were successfully grown from dichloromethane solutions layered with diethyl ether at 255 K or by allowing slow diffusion of diethyl ether onto chloroform solutions at room temperature, respectively. Data collections were carried out at room temperature on a Bruker Smart CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and 20 or 30 mA for **1a** and [**7**]ClO_4, respectively. In both cases data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each exposure of 20 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 exposure, and no appreciable drop in the intensities was observed. A summary of the fundamental crystal data is given in Table 2. The structures were solved by direct methods and conventional Fourier techniques. The refinement was done by full-matrix least-squares on F^2.[36] Anisotropic parameters were used in the last cycles of refinement for all non-H atoms with exceptions. For **1a** the solvent molecule was isotropically refined three cycles and the thermal parameters were kept constant in subsequent cycles while the coordinates were refined with geometric restraints and variable common C−C and C−O distances. For [**7**]ClO_4 the oxygen atoms in the ClO_4 anion have been refined isotropically and after the last cycles of refinement the Fourier difference map showed some residual electronic density, which was assigned to one half disordered Et_2O solvent. All hydrogen atoms were calculated at geometrical positions and refined as riding on their respective C atoms, except the H2A and H2B atoms bonded to the N2 atom in both compounds, which were found in a difference Fourier synthesis and their coordinates and thermal parameters were fixed. These features led to R1 factors of 0.0549 (5194 reflections observed) and 0.061 (3080 reflections observed) for **1a** and [**7**]ClO_4, respectively. The largest residual peak in the final difference map, 1.43 and 0.77 e Å^{-3}, are in the vicinity of the solvent molecule in **1a** and of the ClO_4^- anion in [**7**]ClO_4.

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Supporting Information Available: PLUTO views of **1a** and [**7**]ClO_4 showing the dimer formation. Crystallographic data file of complexes **1a** and [**7**]ClO_4 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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