Hydroxyalkyl Complexes and Hemiaminal Formation in the Reaction of *o*-Diphenylphosphinobenzaldehyde with Rhodium(I) Dihydrazone Complexes

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The diimino complex Rh(COD)(bdh)Cl (bdh: $H_2NN{=}C(Me)C(Me){=}NNH_2$) reacts with *o*-diphenylphosphino(benzaldehyde) (PCHO) in the presence of PPh_3 to give acylhydrido $[Rh(H)(PCO)(PPh_3)(bdh)]^+$ species. When using Rh/PCHO = 1:2 stoichiometric ratios, oxidative addition of one PCHO and P-coordination of another PCHO occurs. The aldehyde group then undergoes two competitive reactions: (i) addition of one free amino group to give a stable hemiaminal and a complex $[Rh(H)(PCO)(Pbdh)]^+$ that contains a new PNN ligand coordinated via the imino nitrogens and the phosphorus atom or (ii) insertion into Rh−H to give the hydroxyalkyl complex $[Rh(PCO)(PCHOH)(bdh)]^+$. The complexes have been fully characterized, and X-ray diffraction structures of both of them are reported. Some intermediates in the competitive reactions have been spectroscopically characterized, and the transformation of the hemiaminal group into imine to give a PaNN ligand in the complex $[Rh(H)(PCO)(Pabdh)]^+$ has also been studied.

Introduction

Organometallic rhodium complexes play an important role in the transformation of many organic compounds.[1] The most studied catalysts are those containing phosphine ligands, and the recent development of homogeneous catalysis shows an increasing interest in using N-donor-containing complexes.[2] Many transformations affecting aldehydes are catalyzed by rhodium complexes and may involve oxidative addition of aldehyde to rhodium(I).[3] Cleavage of C−H bonds in aldehydes and promoted by rhodium may lead to acylhydrido species,[4] and the presence of N-donors gives electron-rich metal centers and may favor the oxidative addition reaction;[5] $[Rh(NP_3)]^+$ species ($NP_3 = N(CH_2CH_2PPh_2)_3$) react with aldehydes to give $[Rh(H)(COR)(NP_3)]^+$, while the isoelectronic species $[Rh(PP_3)]^+$ does not give this reaction.[6−8] When the aldehyde is close to a donor atom and chelates can be formed, the corresponding acylhydrido complexes may be obtained more easily.[7,9] *o*-(Diphenylphosphino)benzaldehyde (PCHO) has been used to add oxidatively to rhodium(I),[7] iridium(I),[10] platinum(0),[11] or cobalt(I),[12] yielding *cis* acylhydrido complexes that contain acylphosphine chelates (PCO); nevertheless, examples of complexes of these metals containing monodentate PCHO ligand are known.[13] The reduction of aldehydes to alcohols and the conversion of syngas to methanol or ethylene glycol may involve either alkoxy or hydroxymethyl intermediates,[14] and both types of compounds are well known for late transition metals.[15,16] Hydrogenation of aldehydes by rhodium phosphine complexes is believed to proceed via hydroxyalkyl intermediates,[17] though insertion of an

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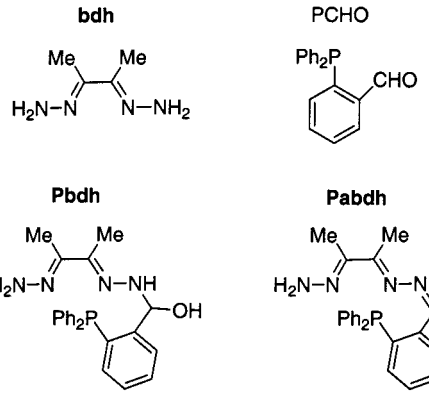
aldehyde into a M−H bond is rarely observed.[16,18] The reaction of $RhH(N_4)$ compounds (N_4 = macrocyclic or nonmacrocyclic ligand) with RCHO gives the hydroxyalkyl $[Rh(CH(OH)R)(N_4)]$ derivatives,[19] and chelate assistance allows PCHO to insert into M−H of $HMn(CO)_5$ to give the hydroxyalkyl derivative $Mn(CO)_4(PPh_2(o\text{-}C_6H_4CHOH))$,[20] while $HPt(PPh_2O)(PPh_2OH)_2$ gives a cyclic platinum alkoxide $Pt(PPh_2O)(PPh_2OH)(PPh_2(o\text{-}C_6H_4CH_2O))$[21] and $[IrH(PCO)Cl(CO)(PPh_2(o\text{-}C_6H_4CHO))]$ contains a monodentate PCHO.[22]

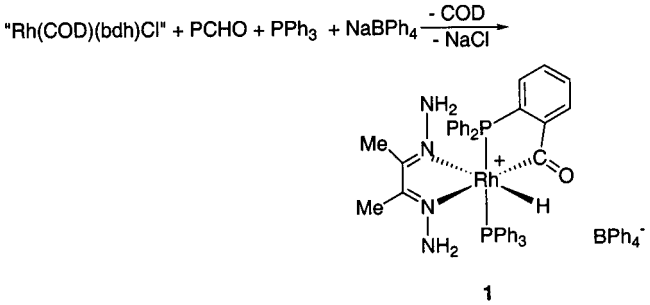
Since its preparation by Rauchfuss,[23] PCHO has been widely used to prepare hemilabile ligands, by condensation of the aldehyde group with primary amines, that are of interest in the synthesis of homogeneous catalysts precursors.[24] Complexes of the isolated bidentate iminophosphines PN,[25] PNN ligands that can behave as tridentates or as PN bidentates,[26] or PPNN tetradentate ligands[27] have been reported. The condensation reaction occurs via hemiaminal >C(OH)NHR intermediates that lose water readily to give the imine group. Some of these hemiaminals have been detected spectroscopically,[28] and recently it has been reported that the coordinated amino group of glycylglycinato Co(III) complexes reacts with formaldehyde in alkaline aqueous solution to give a mixture of coordinated hemiaminal and imino complexes and that the hemiaminal group transforms readily into imine.[29]

In this work we report the reactions of a rhodium(I) compound Rh(COD)(bdh)Cl containing a bidentate diimine ligand such as biacetyldihydrazone (bdh)[30] with PCHO to give the oxidative addition product (Rh/PCHO = 1:1). When using Rh/PCHO = 1:2 stoichiometric ratios, complexes of a new tridentate PNN ligand and hydroxyalkyl complexes are formed in a competitive reaction. Unexpectedly the PNN ligand contains a very stable hemiaminal group. Some of the intermediates in the competitive reaction have been characterized, and the crystal structure of the two isolated compounds is reported. Transformation of the hemiaminal group into imine to give the PaNN ligand has also been studied. Chart 1 shows the ligands used and the new tridentate PNN and PaNN ligands formed.

Chart 1



Scheme 1



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Results and Discussion

Rh/PCHO = 1:1 Reactions. The reaction of Rh(COD)(bdh)Cl prepared "in situ" with *o*-diphenylphosphino(benzaldehyde) (PCHO) (Rh/PCHO = 1:1) requires the presence of PPh_3 (Rh/PPh_3 = 1:1) for all the starting material to react and leads to the chelate-assisted oxidative addition product, with displacement of 1,5-cyclooctadiene, as shown in Scheme 1. The acylhydrido complex formed contains unmodified dihydrazone ligand and has been isolated as the tetraphenylborate salt $[Rh(H)(PCO)(PPh_3)(bdh)]BPh_4$ (**1**), which behaves as 1:1 electrolyte in acetone solution.[31]

The IR spectrum shows the expected absorptions due to coordinated diimines, ν(Rh−H) in the 2000−2030 cm^{-1} region and ν(C=O), ca. 1600 cm^{-1}, at lower frequencies than in the free ligand, indicating acyl coordination.[7,22] The ν(N−H) absorptions due to uncoordinated amino groups are not displaced toward lower frequencies with respect to the free ligands. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets of doublets corresponding to an AMX pattern. PCO shows the characteristic low-field resonance, ca. 60 ppm (J(Rh,P) 128 Hz) due to the five-membered-ring effect.[32] The

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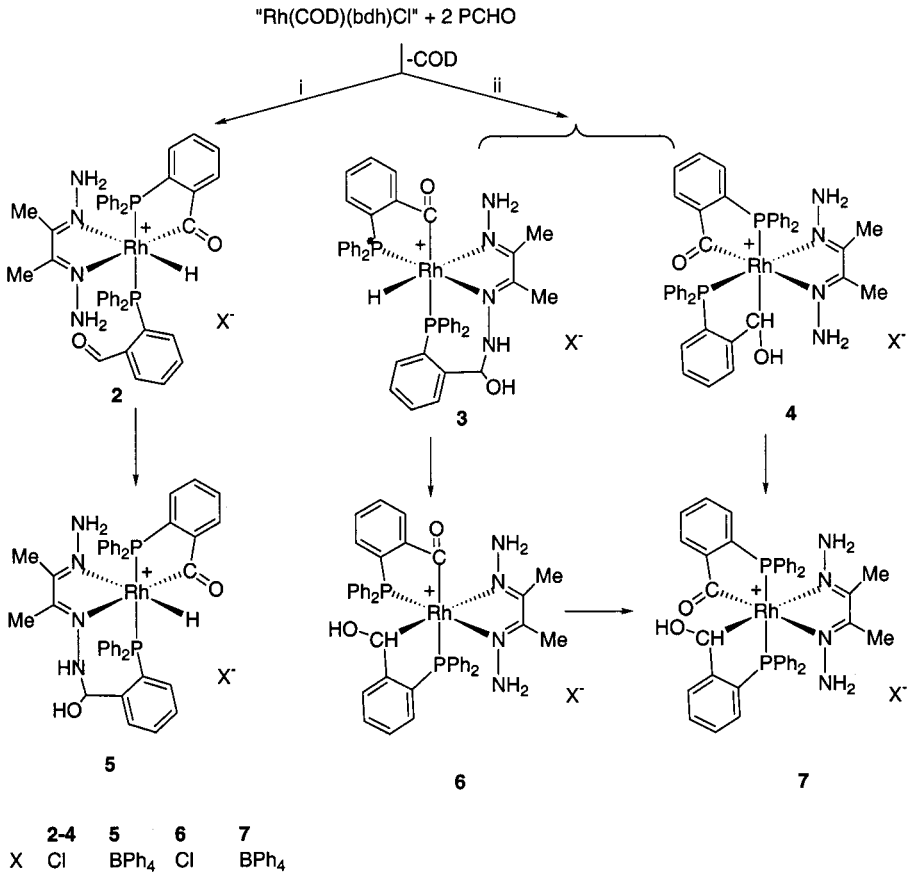
Scheme 2



resonance of coordinated PPh_3 appears around 40 ppm (J(Rh,P) 120 Hz) and J(P,P) of 310 Hz, indicating *trans* arrangement of the phosphorus atoms. The ^{1}H NMR spectrum shows a hydride resonance in the high-field region, ca. −13 ppm, as a multiplet due to a J(Rh,H) of 19 Hz and equals a J(P,H) of 10 Hz, which agree with both phosphines being *cis* to the hydride. The $^{13}C\{^1H\}$ NMR spectrum shows the expected doublet for the acyl group at ca. 240 ppm (J(Rh,C) 30 Hz).[33] The diimine shows two sets of resonances due to inequivalent imino fragments *trans* to hydride or acyl, respectively.

Rh/PCHO = 1:2 Reactions. Rh(COD)(bdh)Cl prepared "in situ" reacts with *o*-diphenylphosphino(benzaldehyde) (PCHO) (Rh/PCHO = 1:2) to undergo the oxidative addition of one PCHO, with displacement of 1,5-cyclooctadiene, and P-coordination of the second PCHO molecule. Its aldehyde then undergoes two competitive reactions as depicted in Scheme 2: (i) addition of one free amino group of the dihydrazone to form a hemiaminal group, thus giving a new PNN tridentate ligand and complex $[Rh(H)(PCO)(Pbdh)]^+$ (**5**), or (ii) insertion into the Rh−H bond to give hydroxyalkyl complexes such as $[Rh(PCO)(PCHOH)(bdh)]^+$ (**7**). The reactions performed in CH_2Cl_2 or CH_3OH gave mixtures of almost equal amounts of hemiaminal-containing species and hydroxyalkyl complexes. By following this reaction in CD_3OD, we have been able to detect some of the intermediates shown in Scheme 2. At 253 K formation of the complexes in **2**−**5** is observed. Both **2** and **5** contain *trans* P atoms, while **3** and **4** contain *cis* P atoms. **2** is a precursor of **5**, while **3** and **4** are involved in the formation of the stable hydroxyalkyl complex (vide infra).

Hemiaminal-Containing Complexes. 2 contains acylphosphine chelate (δPCO 72.8 {dd} ppm, J(Rh,P) 126 Hz), *trans* (J(P,P) 319 Hz) to monodentate PCHO (δPCHO 43.8 {dd} ppm, J(Rh,P) 122 Hz; δHCO 9.42 {s} ppm) and hydride (δH−Rh −12.6 ppm {ddd}, J(Rh,H) 18 Hz, J(PCO,H) 6 Hz, J(PCHO,H) 11 Hz) and transforms at 253 K into the complex in **5**, while the other species remain unmodified. Therefore we think that P-coordination of PCHO occurs prior to hemiaminal formation. When performing this reaction at 293 K, **2** is not observed.

[Rh(H)(PCO)(Pbdh)]Cl precipitates almost quantitatively when the reaction is performed in CH_2Cl_2 and can thus be separated from the reaction mixture. The isolation of $[Rh(H)(PCO)(Pbdh)]BPh_4$ (**5**) allows complete characterization of the complex. To ascertain hemiaminal formation, we have also prepared [Rh(H)-(PCO)(Pgmh)]BPh_4 (**8**) because gmh (MeHNN=CHCH=NNHMe) contains secondary amino groups and cannot undergo condensation to form imine. These compounds behave as 1:1 electrolytes,[31] and their FAB spectra show the corresponding [M$^+$] peak. The appearance of ν(OH) at ca. 3500 cm^{-1} suggests the hemiaminal formation confirmed by NMR spectroscopy. The $^{13}C\{^1H\}$ NMR spectra show the resonance due to >CH(OH)NR″− around 85 ppm (J(P,C) {d} 8 Hz). In the ^{1}H NMR spectrum of **5** (R″ = H) the signals due to NH (5 ppm) and CH (7 ppm) are coupled and appear as doublets (J(H,H) 10 Hz), while OH shows a singlet at ca. 2 ppm.

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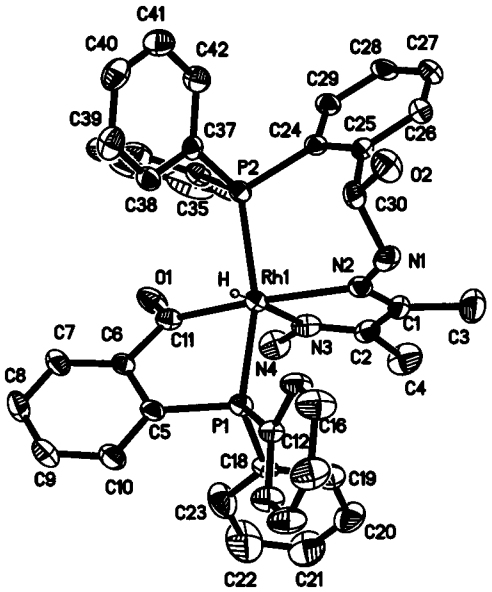

Figure 1. ORTEP view of the cation in **5** showing the atomic numbering (30% probability ellipsoids). The hydrogen atoms except one have been omitted for clarity.

These assignments agree with other reported data,[34] and **8** ($R'' = CH_3$) shows a singlet at 2 ppm due to OH. The ^{31}P resonance of the new tridentate ligand PNN in a seven-membered metallocycle in compound **5** appears around 25 ppm (J(Rh,P) 120 Hz). Other spectroscopic features are similar to those of compound **1** (see Experimental Section) and indicate the presence of only one isomer, which, because hydride chemical shifts are sensitive to the nature of the *trans* groups,[35] we assign tentatively to that containing the hydride *trans* to the unreacted hydrazone group.

An X-ray diffraction study of **5** has been undertaken and confirms hemiaminal formation and the hydride being *trans* to the unreacted hydrazone group. To the best of our knowledge, this is the first crystal structure of a late transition metal complex containing a hemiaminal group. The crystal consists of [Rh(H)(PCO)(Pbdh)] cations and BPh_4 anions held together by electrostatic interactions. Figure 1 shows an ORTEP view of the molecular structure of the cation; pertinent bond distances and angles are summarized in Tables 1 and 2. The N1−C30 and C30−O2 distances, 1.485(7) and 1.417(6) Å, respectively, along with the O2−C30−C25 angle of 110.3(4)° show the new C−N bond formation, with C30 changing from sp^2 to sp^3. As expected, the cation in **5** exhibits a distorted octahedral geometry, due to the presence of the chelate rings, in which the P atoms occupy *trans* positions and the highest deviation of 21° corresponds to the P1−Rh1−P2 angle. Imino N2, N3, and P2 atoms of the PNN ligand occupy three facial positions, the hydride is *trans* to N3 (N3−Rh1−H, 167(1)°), and C11 of the acyl group fills the sixth coordination site. The best least-squares plane C11,N2, N3,H,Rh1 shows a 0.19(5) Å maximum deviation for the H atom. The metallocycle including the acylphosphine chelate Rh1,P1,C5,C6,C11 deviates from planarity and forms a dihedral angle of 18.3(1)° with its phenyl ring.[36] The observed Rh−C(acyl), C=O(acyl), and Rh−P distances fall within reported ranges,[37] and the Rh−N distances are as expected.[30] Rh1−P1 (2.299(1) Å) is shorter than Rh1−P2 (2.348(1) Å), and this may be due to P1 forming a five-membered chelation ring and P2 being in a seven-membered chelate ring that adopts a boat conformation. It has been reported that acyl ligands have slightly weaker *trans*-influence than hydride.[38] In **5** Rh−N2 *trans* to the acyl group is longer than Rh−N3 *trans* to hydride, and this can be due to N2 being the central atom of a tridentate ligand. The Rh−H distance is in the short end of the 1.993−1.245 Å range found for rhodium hydrides (CSD-Database 5.18, October 1999) and is similar to that reported for other Rh(III) complexes.[39] The BPh_4 anion shows the expected angles and distances.

Table 1. Selected Bond Lenghts (Å) for the Complexes [Rh(H)(PCO)(Pbdh)]BPh_4 (5) and [Rh(PCO)(PCHOH)(bdh)]BPh_4 (7)

	5	7
Rh(1)−P(1)	2.299(1)	2.316(1)
Rh(1)−P(2)	2.348(1)	2.356(1)
Rh(1)−N(3)	2.145(5)	2.171(3)
Rh(1)−N(2)	2.181(4)	2.211(3)
Rh(1)−C(11)	1.990(5)	2.004(4)
Rh(1)−C(30)		2.097(4)
Rh(1)−H	1.41(5)	
P(1)−C(5)	1.815(5)	1.805(4)
P(1)−C(18)	1.820(5)	1.827(4)
P(1)−C(12)	1.806(5)	1.832(4)
P(2)−C(24)	1.830(5)	1.821(4)
P(2)−C(31)	1.816(6)	1.834(4)
P(2)−C(37)	1.830(5)	1.838(4)
O(1)−C(11)	1.219(6)	1.219(5)
O(2)−C(30)	1.417(6)	1.440(5)
O(2)−H(2)	1.122	0.814
N(1)−N(2)	1.414(6)	1.389(5)
N(1)−H(1A)	1.093	1.044
N(1)−H(1B)		1.046
N(2)−C(1)	1.304(7)	1.301(5)
N(3)−C(2)	1.288(7)	1.305(5)
N(3)−N(4)	1.363(6)	1.391(4)
N(4)−H(4A)	0.825	0.996
N(4)−H(4B)	0.880	0.854

Table 2. Selected Angles (deg) for the Complexes [Rh(H)(PCO)(Pbdh)]BPh_4 (5) and [Rh(PCO)(PCHOH)(bdh)]BPh_4 (7)

5		7	
C(11)−Rh(1)−H	92(2)	C(11)−Rh(1)−C(30)	84.8(2)
C(11)−Rh(1)−N(3)	96.1(2)	C(11)−Rh(1)−N(3)	97.9(1)
N(3)−Rh(1)−H	168(2)	C(30)−Rh(1)−N(3)	175.3(1)
C(11)−Rh(1)−N(2)	169.3(2)	C(11)−Rh(1)−N(2)	170.5(2)
N(2)−Rh(1)−H	98(2)	C(30)−Rh(1)−N(2)	104.2(2)
N(3)−Rh(1)−N(2)	73.1(2)	N(3)−Rh(1)−N(2)	72.9(1)
C(11)−Rh(1)−P(1)	80.0(2)	C(11)−Rh(1)−P(1)	84.5(1)
P(1) −Rh(1)−H	76(2)	C(30)−Rh(1)−P(1)	88.1(1)
N(3)−Rh(1)−P(1)	96.9(1)	N(3)−Rh(1)−P(1)	88.4(1)
N(2)−Rh(1)−P(1)	100.7(1)	N(2)−Rh(1)−P(1)	92.8(1)
C(11)−Rh(1)−P(2)	91.0(2)	C(11)−Rh(1)−P(2)	90.6(1)
P(2)−Rh(1)−H	86(2)	C(30)−Rh(1)−P(2)	80.4(1)
N(3)−Rh(1)−P(2)	102.0(1)	N(3)−Rh(1)−P(2)	103.4(1)
N(2)−Rh(1)−P(2)	91.5(1)	N(2)−Rh(1)−P(2)	93.8(1)
P(1)−Rh(1)−P(2)	159.86(5)	P(1)−Rh(1)−P(2)	167.80(4)

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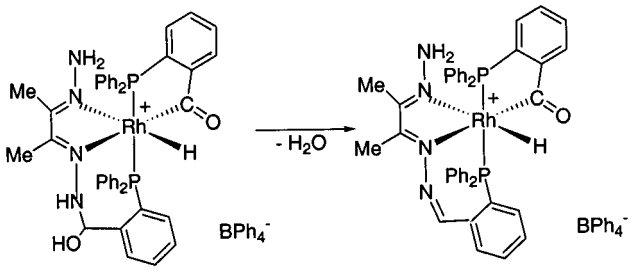
Scheme 3



The uncoordinated HN−CH(OH) hemiaminal group in complex $[Rh(H)(PCO)(Pbdh)]^+$ **5** is stable in the solid state and also in methanol or dichloromethane solution. Condensation reaction of these groups to afford the corresponding imines by hydrogen transfer from N to O is usually easy and needs both H and OH being on the same side of the N−C bond.[40] We think that the hemiaminal in **5** is stable because it belongs to a rather rigid seven-membered metallocycle.[41] Compound **5** in unstabilized chloroform transforms very slowly at room temperature into **9**, which contains a new tridentate PaNN ligand (Scheme 3). The NH and OH resonances disappear, and a new resonance at 1.43 ppm due to H_2O is observed. Addition of HCOOH accelerates the reaction, most likely by protonation of the hydroxy group, though the obtained compound is impure. Compound **9** is also a hydride, and its $^{13}C\{^1H\}$ NMR spectrum shows three singlets due to three different C=N groups. The $^{31}P\{^1H\}$ NMR spectrum shows an AMX pattern with PaNN in **9** at lower field than PNN in the starting complex **5**; therefore we think that **9** contains a tridentate ligand also forming a seven-membered PN and a five-membered NN chelate ring. A shift toward higher fields would be expected if opening of one arm of the tridentate ligand[42] followed by formation of two six-membered metallocycles was to occur.[32]

In refluxing absolute ethanol, cleavage of the hemiaminal group in complex **5** to regenerate the bidentate NN ligand occurs (eq 1), and the new species $[Rh(PCO)_2$-

$$\underset{\mathbf{5}}{[Rh(H)(PCO)(Pbdh)]^+} \xrightarrow{\text{EtOH, reflux}} \underset{\mathbf{10}}{[Rh(PCO)_2(bdh)]^+} + H_2 \quad (1)$$

$(bdh)]^+$ **10** is formed, likely with H_2 loss. According to NMR data **10** contains equivalent phosphine−acyl groups and equivalent imino groups and no hydride. Its FAB spectrum shows the corresponding $[M^+]$ peak and confirms this formulation, although the elemental analysis is not in convenient agreement with the expected values, and this can be due to bad combustion of the sample or to the presence of NMR-silent impurities.

Hydroxyalkyl Complexes. As mentioned above, the reaction of "Rh(COD)(bdh)Cl" with (PCHO) (Rh/PCHO = 1:2) in CD_3OD at 253 K gives species **3** and **4** among others (Scheme 2). Our proposal of structures for both complexes is based on spectroscopic evidence[43] assuming *cis* oxidative-addition of aldehyde.[7] Both **3** and **4** contain two phosphorus atoms mutually *cis* (J(P,P) 13 and 19 Hz, respectively) and no free aldehyde. **3** contains hydride *cis* to both phosphines (δH−Rh −14.46 {ddd} ppm, J(Rh,H) 18, J(P,H) 31, 13 Hz) and due to the absence of aldehyde can contain a hemiaminal group in a PNN ligand with P (δ 17.1 {dd} ppm) *trans* to an acyl group (J(Rh,P) 67 Hz) and P of the acylphosphine chelate (δ 76.3 {dd} ppm) *trans* to N (J(Rh,P) 149 Hz). **4** contains no hydride and shows a broad singlet at 6.68 ppm that can be due to C*H*OH of a hydroxyalkyl group in a PCHOH chelate, with P (δ 59.8 {dd} ppm) *trans* to N (J(Rh,P) 150 Hz) and P of the acylphosphine chelate (δ 40.2 {dd} ppm) *trans* to hydroxyalkyl (J(Rh,P) 82 Hz). On raising the temperature to 293 K, **4** remains unaltered, while **3** transforms into **6**, which contains no hydride and according to its spectral features (δPCO 57.6 {dd} ppm, J(Rh,P) 148, J(P,P) 21 Hz; δPCHOH 38.6 {dd} ppm, J(Rh,P) 80 Hz; δCHOH 6.05 {s} ppm) is an isomer of **4**. These observations suggest cleavage of the hemiaminal group in **3** and insertion of aldehyde into the Rh−H bond to form the hydroxyalkyl group. When performing this reaction at 293 K, a mixture of **4**, **5**, and **6** is formed and **3** is not observed. At room temperature both **4** and **6** rearrange into the final product **7**, containing *trans* phosphines.

When performing this reaction in CH_3OH, addition of $NaBPh_4$ gives a precipitate containing a mixture of **5** and **7**. By refluxing the solid in absolute ethanol, **5** dissolves and is transformed into **10** (eq 1), while highly unsoluble **7** remains solid and can thus be separated from the mixture. $[Rh(PCO)(PCHOH)(bdh)]BPh_4$ (**7**) behaves as 1:1 electrolyte in acetone solution and shows ν(OH) around 3500 cm^{-1}. ^1H and $^{13}C\{^1H\}$ NMR confirm formation of the hydroxyalkyl group bonded to rhodium.[20,44] Its ^{13}C resonance appears at 75.5 ppm (J(Rh,C) {d} 28 Hz), the methine proton at ca. 5 {ddd} ppm is coupled with rhodium (J(Rh,H) 2 Hz), the hydroxy proton (J(H,H) 4 Hz), and phosphorus (J(P,H) 15 Hz), and the hydroxy proton appears as a doublet (ca. 1.7 ppm). The dihydrazone ligand shows two sets of resonances due to inequivalent imino fragments, and the $^{31}P\{^1H\}$ NMR spectrum shows two doublets of doublets (ABX pattern) corresponding to two inequivalent phosphines mutually *trans* (J(P,P) 320 Hz).

The crystal structure of **7** confirms the spectroscopic findings. The crystal consists of [Rh(PCO)(PCHOH)-(bdh)] cations and BPh_4 anions held together by electrostatic interactions. Figure 2 shows an ORTEP view of the molecular structure of the cation; pertinent bond distances and angles are summarized in Tables 1 and 2. The cation in **7** exhibits a distorted octahedral geometry, in which the P atoms occupy *trans* positions, the highest deviation of 13.2° corresponds to the P1−Rh1−P2 angle, and the distortion is less severe than that for **5**. The equatorial plane is occupied by the imino N atoms and the carbon atoms. This best least-squares plane shows a 0.013(4) Å maximum deviation for the

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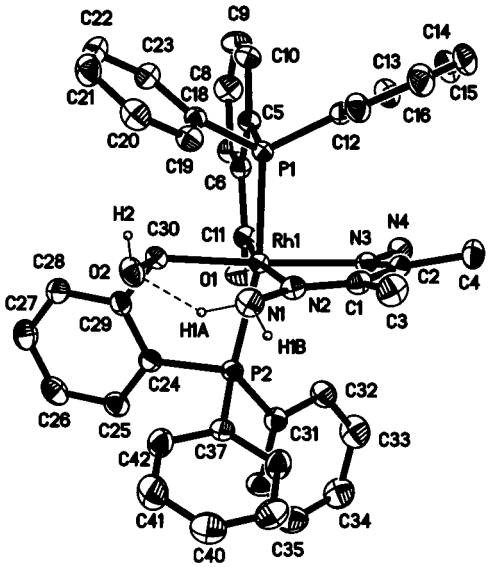

Figure 2. ORTEP view of the cation in **7** showing the atomic numbering (30% probability ellipsoids) and the intramolecular hydrogen bond. The hydrogen atoms except three have been omitted for clarity.

C30 atom, and the rhodium atom is placed out of this plane (0.0589(3) Å).[36] Both P1 and P2 are in five-membered chelation rings. The metallocycle including the acylphosphine chelate Rh1,P1,C5,C6,C11 is almost planar, contrarily to **5**, with a maximum deviation of 0.025(4) Å for C11, and forms a dihedral angle of 0.8(1)° with its phenyl ring. The metallocycle including the hydroxyalkylphosphine chelate deviates from planarity as expected, and the best least-squares plane Rh1,P2,C24,C29,C30 forms a dihedral angle of 34.0(1)° with its phenyl ring. Also, the Rh1−C30 (2.097(4) Å) and the Rh1−P2 (2.356(1) Å) distances are slightly longer than the Rh1−C11 and the Rh1−P1 distances (2.004(4) and 2.316(1) Å, respectively). These differences may be viewed as a consequence of the different hybridization for C30 (sp^3) and for C11 (sp^2).[45] The different Rh1−N2 and Rh1−N3 distances (Table 1) can reflect the suggested slightly larger *trans*-influence of the acyl than of the hydroxyalkyl group[45a] now in the same complex. In addition an intramolecular hydrogen bond between O2 and N1 is observed (N1- - -O2 and O2- - -H1A distances of 2.914(5) and 2.016(3) Å, respectively, and NHO angle 142.5(2)°). Other features of the bdh ligand[30] and the BPh_4 anion are as expected.

Conclusions

A rhodium(I) complex containing biacetyldihydrazone undergoes readily the chelate-assisted oxidative addition of PCHO to give the *cis* acylhydrido complex. A second PCHO molecule may coordinate to rhodium as a P-monodentate ligand and may occupy a *cis* or a *trans* site with respect to the P atom of the acylphosphine. The *trans* disposition allows the reaction of the aldehyde group with one amino group to form a hemiaminal, while the *cis* disposition allows the insertion of aldehyde into the Rh−H bond to form hydroxyalkyl complexes. The hemiaminal is stable because it is included in a seven-membered metallocycle, and its transformation into azines is favored by acids.

Experimental Section

General Procedures. The preparation of the metal complexes was carried out at room temperature under nitrogen by standard Schlenk techniques. [{Rh(COD)Cl}$_2$][46] was prepared as previously reported. α-Diimines[47] were synthesized according to known procedures. *o*-Diphenylphosphine(benzaldehyde) (PCHO) was purchased from Aldrich and used as received. Microanalysis were carried out with a Leco CHNS-932 microanalyzer. Conductivities were measured in acetone or methanol solution with a Metrohm E 518 conductimeter. IR spectra were recorded with a Nicolet FTIR 740 spectrophotometer in the range 4000−400 cm^{-1} using KBr pellets. NMR spectra were recorded with an XL-300 Varian spectrometer; ^1H and ^{13}C (TMS internal standard) and ^{31}P (H_3PO_4 external standard) spectra were measured from $CDCl_3$, CD_3OD, 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).

[[Rh(H)(PCO)(PPh_3)(bdh)]BPh_4 (1). To a MeOH suspension of [{Rh(COD)Cl}$_2$] (0.04 mmol) were added stoichiometric amounts (0.08 mmol) of bdh, PPh_3, and PCHO, whereupon a brown solution was formed, which upon addition of $NaBPh_4$ (0.08 mmol) gave a precipitate that was filtered off, washed with MeOH, and vacuum-dried. Yield: 60%. IR (KBr, cm^{-1}): 3394(s), 3288(s), ν(NH_2); 2020(w), ν(RhH); 1612(s), ν(C═O); 1576(s), ν(C═N). Λ_M (Ω^{-1} cm^2 mol^{-1}): 72 (acetone). FAB MS: calcd for $C_{41}H_{40}N_4OP_2{}^{103}Rh$, 769; observed, 769 ($M^+$). ^1H NMR ($CDCl_3$): δ −12.88 (m, RhH), J(Rh,H) 19, J(P,H) 10; 4.64 (s), 4.54 (s) (NH_2); 0.87 (s), 0.86 (s) (CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.4 (dd, PCO), J(Rh,P) 128, J(P,P) 313; 42.3 (dd, PPh_3), J(Rh,P) 120. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 243.3 (d, CO), J(Rh,C) 31; 149.3 (s), 147.8 (s) (C═N); 12.6 (s), 12.9 (s) (CH_3). Anal. Calcd for $C_{65}H_{60}BN_4OP_2Rh$: C, 71.70; H, 5.55; N, 5.15. Found: C, 71.31; H, 5.21; N, 4.86.

[Rh(H)(PCO)(Pbdh)]BPh_4 (5). To a CH_2Cl_2 solution of [{Rh(COD)Cl}$_2$] (0.04 mmol) was added a stoichiometric amount (0.08 mmol) of bdh, whereupon a red precipitate was formed, which upon addition of PCHO (0.16 mmol) gave a yellow solution, from which a yellow precipitate of [Rh(H)(PCO)(Pbdh)]Cl appeared that was filtered off and dried (50% yield). [Rh(H)(PCO)(Pbdh)]Cl (0.06 mmol) was dissolved in MeOH, and $NaBPh_4$ (0.06 mmol) was added to give a precipitate that was filtered off, washed with MeOH, and vacuum-dried. Yield: 80%. IR (KBr, cm^{-1}): 3535(m), ν(OH); 3401(m), 3302(m), ν(NH_2); 2048(w), ν(RhH); 1607(s), ν(C═O); 1576(s), ν(C═N). Λ_M (Ω^{-1} cm^2 mol^{-1}): 86 (acetone). FAB MS: calcd for $C_{42}H_{40}N_4O_2P_2{}^{103}Rh$, 797; observed, 797 ($M^+$). ^1H NMR ($CDCl_3$): δ −12.86 (m, HRh), J(Rh,H) 19, J(P,H) 10; 7.34 (d, HC−N), ^3J(H,H) 10; 5.16 (d, NH); 4.72 (s, NH_2); 2.27 (s, OH); 0.92 (s), 0.75 (s) (CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 62.1 (dd, PCO), J(Rh,P) 126, J(P,P) 311; 26.6 (dd, PNN), J(Rh,P) 120. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 238.6 (d, CO), J(Rh,C) 31; 148.6 (s), 148.0 (s) (C═N); 84.6 (d, COH), J(P,C) 8; 13.3 (s), 12.0 (s) (CH_3). Anal. Calcd for $C_{66}H_{60}BN_4O_2P_2Rh$: C, 70.98; H, 5.41; N, 5.02. Found: C, 70.59; H, 5.25; N, 5.04.

[Rh(PCO)(PCHOH)(bdh)]BPh_4 (7). To a MeOH suspension of [{Rh(COD)Cl}$_2$] (0.12 mmol) were added stoichiometric amounts of bdh (0.24 mmol) and PCHO (0.48 mmol). After 24 h stirring at room temperature the volatiles were removed in a vacuum and the residue was dissolved in EtOH. Addition of

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Table 3. Crystal and Refinement Data for [Rh(H)(PCO)(Pbdh)]BPh_4 (5) and [Rh(PCO)(PCHOH)(bdh)]BPh_4 (7)

	5	7
formulas	$C_{66}H_{60}BN_4O_2P_2Rh$	$C_{66}H_{60}BN_4O_2P_2Rh$
M_r	1116.84	1116.84
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	*P*21/*c*
a, Å	22.400(1)	11.0040(2)
b, Å	15.443(1)	23.7755(2)
c, Å	32.158(2)	21.5596(4)
β (deg)	95.021(2)	99.713(1)
V, Å^3, *Z*	11082(1), 8	5559.7(2), 4
F(000)	4640	2320
D(calcd), g cm^{-3}	1.34	1.334
temp, K	293	293
μ, mm^{-1}	0.42	0.41
cryst dimens, mm	0.11 × 0.11 × 0.09	0.45 × 0.40 × 0.20
diffractometer	Bruker-CCD	Bruker-CCD
radiation	graphite-monochromated Mo Kα (0.71073 Å)	graphite-monochromated Mo Kα (0.71073 Å)
scan technique	ω and φ	ω and φ
data collected	(−23,−20,−42) to (29,17,35)	(−9,−31,−28) to (14,31,27)
θ	1.27−27.92	1.29−28.30
no. of reflns collected	29 241	37 302
no. of ind reflns	12 120 (R_{int} = 0.087)	13 670 (R_{int} = 0.059)
structure solution	Patterson and Fourier	Patterson and Fourier
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/params	12 120/694	13 670/691
$R = \sum[\|F_o\| - \|F_c\|]/\sum\|F_o\|$	0.048 (4709 obs rflns)	0.050 (8934 obs rflns)
R_{wF}[a] (all data)	0.16	0.17
GOF(F^2)	0.75	0.72
maximum residual, e Å^{-3}	0.47	0.43

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

$NaBPh_4$ (0.24 mmol) gave a mixture of **5** and **7**, which was refluxed for 4 h to allow dissolution of **5**. The suspension was filtered warm, and the solid was washed with warm EtOH and vacuum-dried. Yield: 45%. IR (KBr, cm^{-1}): 3542(m), ν(OH); 3408(m), 3373(m), 3295(w), $\nu(NH_2)$; 1626(s), ν(C═O); 1577(s), ν(C═N). Λ_M (Ω^{-1} cm^2 mol^{-1}): 102 (acetone). FAB MS: calcd for $C_{42}H_{40}N_4O_2P_2{}^{103}Rh$, 797; observed, 797 ($M^+$). ^{1}H NMR ($CDCl_3$): δ 5.22 (ddd, *H*C−OH), ^3J(H,H) 4, ^2J(Rh,H) 3, ^4J(P,H) 15; 5.83 (s), 5.07 (s) (NH_2); 1.69 (d, OH); 1.49 (s), 1.34 (s) (CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 57.1 (dd, P_A), J(Rh,P) 128, J(P,P) 323; 49.9 (dd, P_B), J(Rh,P) 132. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 236.9 (d, CO), J(Rh,C) 35; 149.5 (s), 146.5 (s) (C═N); 75.5 (d, CHOH), J(Rh,C) 28; 13.6 (s), 13.3 (s) (CH_3). Anal. Calcd for $C_{66}H_{60}BN_4O_2P_2Rh$: C, 70.98; H, 5.41; N, 5.02. Found: C, 70.49; H, 5.29; N, 4.78.

[Rh(H)(PCO)(Pgmh)]BPh_4 (8). PCHO (0.16 mmol) and gmh (0.08 mmol) were added to a stirring solution of [{Rh(COD)Cl}$_2$] (0.04 mmol) in benzene, and the resulting suspension was filtered after 3 h of stirring. The solid was dissolved in methanol, and addition of $NaBPh_4$ (0.08 mmol) gave a precipitate that was filtered off, washed with MeOH, and vacuum-dried. Yield: 65%. IR (KBr, cm^{-1}): 3492(m), ν(OH); 3358(m), $\nu(NH_2)$; 2055(w), ν(RhH); 1624(s), ν(C═O); 1579(s), ν(C═N). Λ_M (Ω^{-1} cm^2 mol^{-1}): 106 (acetone). FAB MS: calcd for $C_{42}H_{40}N_4O_2P_2{}^{103}Rh$, 797; observed, 797 ($M^+$). ^{1}H NMR ($CDCl_3$): δ −13.11 (m, HRh), J(Rh,H) 21, J(P,H) 10; 5.79(s), 5.74(s) (HC−N); 6.04 (q, NHMe), ^3J(H,H) 4.3; 2.0 (s, OH); 2.04 (s, CH_3), 1.97 (d, MeNH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 56.1 (dd, PCO), J(Rh,P) 126, J(P,P) 311; 25.5 (dd, PNN), J(Rh,P) 118. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 240.1 (d, CO), J(Rh,C) 30; 139.0 (s), 138.9 (s) (C═N); 86.4 (d, COH), J(P,C) 6; 33.1 (s), 31.2 (s) (CH_3). Anal. Calcd for $C_{66}H_{60}BN_4O_2P_2Rh$: C, 70.98; H, 5.41; N, 5.02. Found: C, 70.44; H, 5.31; N, 4.87.

[Rh(H)(PCO)(Pabdh)]BPh_4 (9). A solution of **5** (0.04 mmol) in $CDCl_3$ was allowed to stir for 15 days. Addition of diethyl ether gave a yellow precipitate that was filtered off, washed with diethyl ether, and vacuum-dried. Yield: 51%. IR (KBr, cm^{-1}): 3380(m), 3295(m), $\nu(NH_2)$; 2041(m), ν(RhH); 1590(s), ν(C═O); 1577(s), ν(C═N). Λ_M (Ω^{-1} cm^2 mol^{-1}): 98 (acetone). FAB MS: calcd for $C_{42}H_{38}N_4OP_2{}^{103}Rh$, 779; observed, 779 ($M^+$). ^{1}H NMR ($CDCl_3$): δ −12.92 (ddd, HRh), J(Rh,H) 20, J(PCO,H) 13, J(PaNN,H) 7; 5.14 (s, NH_2); 1.47 (s), 0.59 (s) (CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 61.6 (dd, PCO), J(Rh,P) 128, J(P,P) 307; 34.6 (dd, PaNN), J(Rh,P) 119. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 241.5 (d, CO), J(Rh,C) 30; 157.3 (s), 151.5 (s), 145.2 (s) (C═N); 16.1 (s), 11.5 (s) (CH_3). Anal. Calcd for $C_{66}H_{58}BN_4OP_2Rh\cdot 0.3CHCl_3$: C, 70.18; H, 5.18; N, 4.94. Found: C, 69.68; H, 5.15; N, 4.99.

[Rh(PCO)$_2$(bdh)]BPh_4 (10). A solution of [Rh(H)(PCO)(Pbdh)]Cl (0.09 mmol) in absolute ethanol was refluxed for 4 h. Addition of $NaBPh_4$ (0.09 mmol) gave a brownish precipitate, which was filtered off, washed with ethanol, and vacuum-dried. Yield: 50%. IR (KBr, cm^{-1}): 3394(m), 3295(m), $\nu(NH_2)$; 1594(s), ν(C═O); 1576(s), ν(C═N). Λ_M (Ω^{-1} cm^2 mol^{-1}): 89 (acetone). FAB MS: calcd for $C_{42}H_{38}N_4O_2P_2{}^{103}Rh$, 795; observed, 795 ($M^+$). ^{1}H NMR ($CDCl_3$): δ 4.70 (s, NH_2); 0.74 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 55.2 (d), J(Rh,P) 137. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 236.9 (d, CO), J(Rh,C) 32; 148.5 (s, C═N); 12.8 (s, CH_3). Anal. Calcd for $C_{66}H_{58}BN_4O_2P_2Rh$: C, 71.10; H, 5.24; N, 5.03. Found: C, 66.86; H, 4.86; N, 4.95.

X-ray Structure Determination of 5 and 7. Prismatic yellow single crystals of **5** and **7** were grown by layering dichloromethane solutions with diethyl ether. A summary of the fundamental crystal data and refinement parameters is given in Table 3. The data were collected on a Bruker Smart CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073) radiation operating at 50 kV and 20 mA. 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 cell parameters were determined and refined by least-squares fit of all reflections collected. The structures were solved by Patterson (Rh atoms, SHELXS) and conventional Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXTL).[48] Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were included in calculated positions and

refined as riding on carbon atoms with some exceptions. In both compounds the hydrogen atoms of the amine groups, the alcoholic group, and the hydrogen bonded to C30 were located in a Fourier synthesis, included, and refined isotropically. For **5** the hydride atom has been located as the first peak in a Fourier synthesis and included, and their parameters were refined. Maximum and minimum peaks in the final difference synthesis were 0.43 and −0.49 or 0.47 and −0.34 for **7** and **5**, respectively.

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Acknowledgment. Partial financial support by UPV and Diputación Foral de Guipuzcoa is gratefully acknowledged.

Supporting Information Available: Tables of structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and torsion angles for complexes **5** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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