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Reaction of $[RhCl(CO)_2]_2$ or $[RhCl(COD)]_2$ with *o*-(diphenylphosphino)benzaldehyde. Formation of hemiaminals in the subsequent reaction with dihydrazones

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Abstract

$[RhCl(CO)_2]_2$ reacts with *o*-(diphenylphosphino)benzaldehyde (PCHO) to afford a monocarbonylated rhodium(I) complex containing P-monodentate PCHO, *trans*-$[RhCl(CO)(PCHO)_2]$ (**1**) while $[RhCl(COD)]_2$ undergoes the oxidative addition of one PCHO, with displacement of 1,5-cyclooctadiene, and coordination of the second PCHO molecule as P-(σ-aldehyde) chelate to give [RhH(PCO)Cl(PCHO)] (**2**) which contains *trans* P-atoms. Compound **2** reacts with $H_2NN{=}CHCH{=}NNH_2$ (gdh) to give selectively a complex $[RhH(PCO)(Pgdh)]^+$ containing a stable hemiaminal in a new tridentate ligand, Pgdh, coordinated via the imino nitrogens and the phosphorus and the atom. The reaction of Rh(COD)(gdh)Cl with PCHO gives a mixture of the hemiaminal containing compound and the hydroxyalkyl complex $[Rh(PCO)(PCHOH)(gdh)]^+$ which contains *trans* P-atoms and is formed from precursors containing *cis* P-atoms. The transformation of the hemiaminal group in $[RhH(PCO)(PNN)]^+$ (PNN = Pgdh or Ppvdh (pvdh, $H_2NN{=}CHC(CH_3){=}NNH_2$)) into imine to give new tridentate PaNN ligands in complexes $[RhH(PCO)(PaNN)]^+$ has also been studied.

Keywords: Aldehydes; Oxidative-addition; Rhodium complexes; Hemiaminals

1. Introduction

Organometallic rhodium complexes play an important role in the transformation of many organic compounds [1] and the most studied catalysts are those containing phosphine ligands. Many transformations involving aldehydes such as decarbonylation, hydroacylation, hydrosilylation, hydrogenation or hydroformylation are catalysed by rhodium complexes and may involve oxidative addition of aldehyde to rhodium(I) [2]. Cleavage of C–H bonds in aldehydes and promoted by rhodium may lead to acylhydride species [3–6]. When the aldehyde is close to a donor atom and chelates can be formed, the corresponding acylhydride complexes are easily obtained [5,7] and some of them are active catalysts in the hydroacylation of olefins [7,8]. The reaction of $[IrCl(COD)]_2$ with *o*-(diphenylphosphino)benzaldehyde (PCHO) gives the thermally unstable [IrH(PCO)Cl(COD)] that has been proposed as model intermediate in this process [9] and $[RhCl(1,4\text{-pentanediene})]_2$ reacts with 8-quinolinecarbaldehyde (NCHO) to give an allyl compound $[RhCl(\eta^3\text{-1-ethyl-allyl})(NCO)]_2$ most likely via an acylhydride diolefin intermediate [RhH(NCO)Cl(1,4-pentanediene)] [10]. PCHO has been used to add oxidatively to rhodium(I) [5], iridium(I) [9] platinum(0) [11] or cobalt(I) [12] yielding *cis* acylhydride complexes that contain acylphosphine chelates (PCO). It can also coordinate as monodentate P-donor as in $[Rh(CO)(PCHO)(\mu\text{-pz})]_2$ (pz = pyrazolato ligand) [13], [IrH(PCO)Cl(CO)(PCHO)] that contains the acylhydride fragment and a monodentate PCHO [14] or $[NBu_4]_2{\cdot}[Pt(C_6F_5)_3(PCHO)]$ [15]. This ligand can also behave as chelating phosphine-aldehyde with the aldehyde portion bonded through oxygen (σ-complex) as in $RuCl_2(PCHO)_2$ [9] or $Re(Cl)(CO)_3(PCHO)$ [16] or through both oxygen and carbon (π-complex) as in $Co(C_5Me_5)(PCHO)$ [17] and both bonding modes are well known for aldehyde complexes of transition metals [18], though few rhodium aldehyde derivatives have

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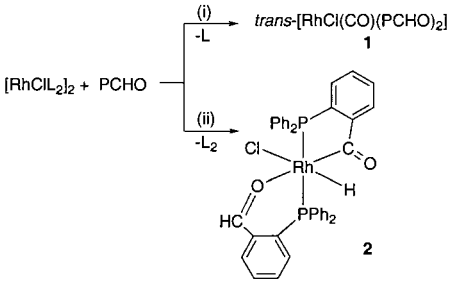
been reported [19]. PCHO has been widely used to prepare hemilabile ligands, by condensation of the aldehyde group with primary amines, which are of interest in the synthesis of homogeneous catalysts precursors [20]. The condensation reaction occurs via hemiaminal >C(OH)NHR intermediates that lose water readily to give the imine group. Some of these hemiaminals have been detected spectroscopically and recently we have reported that Rh(COD)(bdh)Cl (bdh, $H_2NN{=}C(CH_3)$-$C(CH_3){=}NNH_2$) reacts with PCHO to give a mixture of two compounds, a hydroxyalkyl derivative $[Rh(PCO)(PCHOH)(bdh)]^+$, and an acylhydride complex $[RhH(PCO)(Pbdh)]^+$ that also contains a stable hemiaminal group in a new tridentate ligand (Pbdh) formed by reaction of aldehyde and the pendant amino group of coordinated bdh [21]. We report now on the reaction of $[RhCl(CO)_2]_2$ or $[RhCl(COD)]_2$ with PCHO to give, respectively, carbonylated Rh(I) or acylhydride Rh(III) compounds that contain *trans* P-atoms. The reaction of the Rh(III) complex with glyoxaldihydrazone (gdh) to give selectively a stable hemiaminal containing complex and the transformation of the hemiaminal group into imine are also reported.

2. Results and discussion

2.1. Reaction of $[RhClL_2]_2$ with PCHO ($L = CO$; $L_2 = COD$)

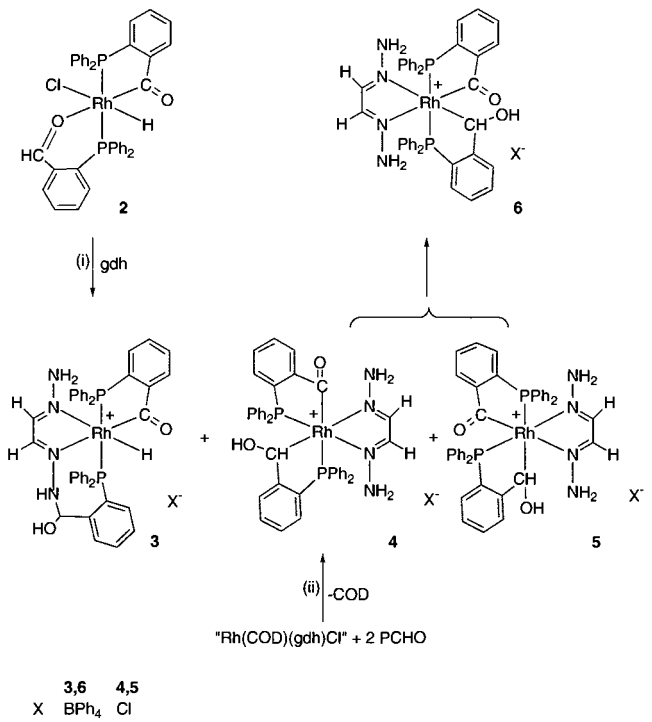
$[RhCl(CO)_2]_2$ reacts with *o*-(diphenylphosphino)-benzaldehyde (PCHO) (Rh–PCHO = 1:2) in benzene to afford a monocarbonylated rhodium(I) complex containing P-monodentate PCHO, *trans*-$[RhCl(CO)(PCHO)_2]$ (**1**) (Scheme 1i) that shows a strong band due to $\nu(C{\equiv}O)$ at 1971 cm^{-1}. IR and NMR spectroscopy confirm monodentate coordination of two equivalent PCHO. $\nu(C{=}O)$, $\delta(\underline{H}CO)$ and $\delta(H\underline{C}O)$ are almost unmodified with respect to the free ligand. The $^{31}P\{^1H\}$-NMR spectrum shows only a doublet due to equivalent phosphine groups bonded to rhodium and consequently the resonance of the C≡O group is a doublet of triplets. J(Rh,C) is as expected [22] and J(P,C) is consistent with both phosphines being *cis* to the carbonyl group. In this reaction no oxidative addition of PCHO is observed. The CO ligand strongly favours low oxidation states and aldehyde C–H bonds are not strong electrophiles. Other carbonylated rhodium(I) compounds have been found to react with PCHO also to give rhodium(I) species with P-monodentate PCHO [13].



Scheme 1. $[RhCl(COD)]_2$ reacts with PCHO (Rh–PCHO = 1:2) in benzene to undergo the oxidative addition of one PCHO, with displacement of 1,5-cyclooctadiene, and coordination of the second PCHO molecule as P-(σ-aldehyde) chelate to give [RhH-(PCO)Cl(PCHO)] (**2**) as shown in (ii).

Compound **2** is stable as a solid and also in toluene solution but decomposes readily in dichloromethane or methanol solution and behaves as non-electrolyte in acetone solution. Its IR spectrum shows the expected ν(Rh–H) absorption at 2041 cm^{-1} and two absorptions due to $\nu(C{=}O)$ in the 1700–1600 cm^{-1} region, at lower frequencies than in the free ligand, indicating acyl coordination of PCO [5,14] and σ-aldehyde coordination of PCHO [9,16,18a]. Despite considerable effort, X-ray quality crystals of **2** could not be obtained although the NMR spectra at 223 K (toluene-d_8) allow its unambiguous characterisation. The $^{31}P\{^1H\}$-NMR spectrum shows two doublets of doublets corresponding to an AMX pattern. PCO shows the characteristic low field resonance, ca. 55 ppm (J(Rh,P) 138 Hz) due to the five-membered ring effect [23] the resonance of PCHO, around 26 ppm (J(Rh,P) 137 Hz), may be consistent with the formation of a six-membered chelate and J(P,P) of 384 Hz, agrees with *trans* arrangement of the phosphorus atoms. The ^{1}H-NMR spectrum shows a sharp singlet due to σ-coordinated aldehyde at slightly higher fields than in the free ligand [17,19] and the hydride resonance in the high field region, ca. −13 ppm, shows coupling to rhodium (J(Rh,H) 28 Hz) and to two inequivalent phosphines *cis* to the hydride (J(P,H) 6 and 10 Hz). Since hydride chemical shifts are sensitive to the nature of the *trans* groups [24], we believe that in complex **2** the hydride is *trans* to chloride as in $[RhClH_2(Ph_2PCH_2CH_2OMe)_3]$ that shows the hydride *trans* to chloride at −15.2 ppm [25]. Hydride *trans* to oxygen appears around −25 ppm as in $[Rh(\eta^2\text{-sulfonato})H_2L_2]$ [26]. The σ-aldehyde bonding of PCHO in **2** containing two electron donating phosphine ligands contrasts with the π-aldehyde bonding reported for $Co(C_5Me_5)(PCHO)$ [17] and can be related to the higher oxidation state shown by the metal in the rhodium(III) compound [27].

Warming the toluene-d_8 solution results in broadening of the hydride resonance so that at room temperature an extremely broad signal is observed while neither the aldehyde resonance nor the $^{31}P\{^1H\}$ spectrum are modified. These observations can be explained by transient formation of a hydroxycarbene tautomer [28,29], reductive elimination/oxidative addition of HCl or re-



Scheme 2.

ductive elimination/oxidative addition involving the acylhydride fragment occurring faster than ^{31}P relaxation. We were unable to observe any resonance at lower field due to the hydroxycarbene proton in the 223–293 K range. Upon addition of Et_3N to a toluene-d_8 solution of **2** at 223 K the complex remains unaltered though on raising the temperature the hydride resonance disappears and a complex mixture of unidentified species is formed. Therefore, we believe that the broadening of the hydride resonance is due to a fast reductive elimination/oxidative addition of HCl.

2.2. Hemiaminal formation

[RhH(PCO)Cl(PCHO)] (**2**), which contains *trans* phosphine groups, reacts in benzene with gdh, $H_2NN{=}CHCH{=}NNH_2$ (gdh) to give species **3** as a unique reaction product (Scheme 2i). The diimine displaces both chloride and σ-aldehyde which reacts with the pendant amino group of the dihydrazone to form a hemiaminal group and the new tridentate ligand Pgdh. $[RhH(PCO)(Pgdh)]^+$ (**3**) has been fully characterised as the tetraphenylborate salt (see Section 3), behaves as 1:1 electrolyte in acetone solution [30] and its FAB spectrum shows the corresponding $[M^+]$ peak. The appearance of ν(OH) at ca. 3500 cm^{-1} and the resonances at 2.16 (s, OH), 5.09 (d, NH) and 6.78 (d, CH) ppm indicate the hemiaminal formation and the ^{31}P{^{1}H}-NMR spectrum shows an AMX pattern with *trans* arrangement of the phosphorus atoms. In **3** both δ^{31}PCO and δ^{31}Pgdh (60.1 and 25.0 ppm, respectively) and also the hydride resonance (-13.19 ppm) appear at slightly higher field than in the related compound derived from biacetyldihydrazone, $[RhH(PCO)(Pbdh)]^+$, with methyl groups as imino C-substituents, which shows δ^{31}PCO and δ^{31}Pbdh at 62.1 and 26.6 ppm, respectively, and δ^1H–Rh at -12.86 ppm [21].

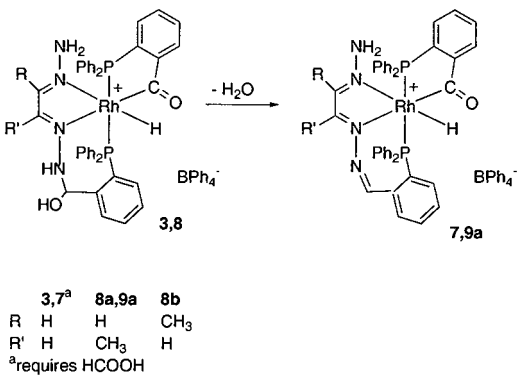
To ascertain that the selective hemiaminal formation is a consequence of the *trans*-disposition of the phosphorus atoms in the starting material we have studied the reaction of Rh(COD)(gdh)Cl [31] prepared 'in situ' with PCHO that gives a mixture of the hemiaminal-containing species, $[RhH(PCO)(Pgdh)]^+$ (**3**) and hydroxyalkyl derivatives $[Rh(PCO)(PCHOH)(gdh)]^+$ (ii). By following this reaction in CD_3OD we have been able to observe the initial formation of **3**, and two hydroxyalkyl intermediates **4** and **5** containing *cis* phosphorus atoms. Compound **4** contains P of the acylphosphine chelate *trans* to N and P of the PCHOH chelate trans to acyl (δPCO 57.6 {dd} ppm, J(Rh,P) 150, J(P,P) 21 Hz; δPCHOH 37.1 {dd} ppm, J(Rh,P) 82 Hz; δCHOH 6.03 {s} ppm) while **5** contains P of the PCHOH chelate *trans* to N and P of the acylphosphine chelate *trans* to hydroxyalkyl (δPCO 38.3 {dd} ppm, J(Rh,P) 85, J(P,P) 19 Hz; δPCHOH 60.2 {dd} ppm, J(Rh,P) 153 Hz). Compounds **4** and **5** rearrange with time into the *trans* derivative **6**. By using dichloromethane or methanol as solvents, complexes **3** and **6** can be separated from the reaction mixtures, [RhH(PCO)(Pgdh)]Cl precipitates when the reaction is performed in CH_2Cl_2 while [Rh(PCO)(PCHOH)(gdh)]Cl is only partially soluble in MeOH.

Compound **6** has been fully characterised as the tetraphenylborate salt $[Rh(PCO)(PCHOH)(gdh)]BPh_4$. It behaves as 1:1 electrolyte in acetone solution and shows ν(OH) around 3500 cm^{-1}. ^{1}H-NMR confirms the formation of the hydroxyalkyl group bonded to rhodium [32]. The dihydrazone ligand shows two sets of resonances due to inequivalent imino fragments and the ^{31}P{^{1}H}-NMR spectrum shows two doublets of doublets (ABX pattern) corresponding to two inequivalent phosphines mutually *trans* (J(P,P) 320 Hz).

The uncoordinated HN–CH(OH) hemiaminal group in $[RhH(PCO)(Pgdh)]^+$ **3**, being included in a rather rigid seven-membered metallocycle, fails to undergo easily the condensation reaction to give the imine, hydrogen transfer from N to O to allow water elimination needs both H and OH being on the same side of the N–C bond [33]. Compound **3** is stable in the solid state and also in unstabilized chloroform for long periods, over 15 days. This was unexpected, because, related $[RhH(PCO)(Pbdh)]^+$, containing methyl groups as imino C-substituents undergoes the condensation reaction at room temperature in unstabilized chloroform, though slowly [21] and suggests that when the

fragment RC=N–NH–CH(OH) contains R: CH_3 the azine formation reaction is easier. The condensation reaction in **3** occurs upon addition of HCOOH that traps the released water, thus shifting the equilibrium to the imine, and forms $[RhH(PCO)(Pagdh)]^+$ **7** (Scheme 3), though the obtained compound is impure. The hydride and the P-resonances of **3** disappear while new signals due to **7** appear (δ^1H–Rh −12.82 {ddd} *J*(Rh,H) 20, *J*(PCO,H) 12, *J*(Pagdh,H) 8; δ^{31}PCO 58.8 {dd} *J*(Rh,P) 126, *J*(P,P) 297; δ^{31}Pagdh 34.4 {dd} J(Rh,P) 117). The shift towards lower fields of the P-resonance of the tridentate ligand on going from **3** to **7** suggests that **7** also contains a tridentate ligand forming a seven-membered PN [23] and a five-membered NN chelate ring.

To confirm the influence of the imino C-substituents in the azine formation reaction, we have prepared a hemiaminal containing complex using pyruvaldihydrazone, $H_2NN{=}CHC(CH_3){=}NNH_2$ (pvdh). The reaction of Rh(COD)(pvdh)Cl [31], prepared 'in situ' in dichloromethane, with PCHO gives a precipitate of [RhH(PCO)(Ppvdh)]Cl. The complex has been characterised as the tetraphenylborate salt (**8**) and is a mixture of two isomers due to hemiaminal formation using the $–C(CH_3){=}NNH_2$ fragment, **8a**, or the $–CH{=}NNH_2$ fragment, **8b** (see Scheme 3). The NMR spectra show the presence of both isomers in ca. 1/2 ratio, two hydride resonances and four doublets of doublets in the $^{31}P\{^1H\}$-NMR are observed. Due to the sensitivity of the hydride chemical shifts to the nature of the *trans* groups [24], we assign the resonance at lower field to the more abundant isomer **8b**. We find now that δ^{31}PCO appears to be sensitive to the nature of the imino group *trans* to the acyl group, so that the presence of methyl C-substituents makes the corresponding resonance to appear at slightly lower fields, δ^{31}PCO(**8a**) > δ^{31}PCO(**8b**). The dissolution of **8** in unstabilized choroform, in the absence of HCOOH, leads to the slow transformation of isomer **8a**, containing the hemiaminal group derived from acetyl, into **9a** (δ^{31}PCO 62.5 {dd} *J*(Rh,P) 126, *J*(P,P) 306; δ^{31}Papvdh 32.9 {dd} *J*(Rh,P) 119) while isomer **8b** remains unmodified (Scheme 3). This observation confirms that the condensation reaction of hemiaminals included in seven-membered metallocycles to form azines is favoured by the presence of methyl substituents in the imino fragment. It has been reported that by increasing the number of methyl groups as C-substituents in coordinated dihydrazones, the intraligand repulsion effects also increase [31,34], therefore we think that the presence of the methyl group makes the seven-membered ring to adopt a more suitable conformation to favour the hydrogen transfer from N to O and hence the condensation reaction.



	3,7[a]	8a,9a	8b
R	H	H	CH_3
R'	H	CH_3	H

[a]requires HCOOH

Scheme 3.

3. Experimental

The preparation of the metal complexes was carried out at room temperature (r.t.) under nitrogen by standard Schlenk techniques. $[RhCl(COD)]_2$ and $[RhCl(CO)_2]_2$ [35] were prepared as previously reported. α-Diimines [34,36] were synthesised according to known procedures. *o*-(Diphenylphosphino)benzaldehyde (PCHO) was purchased from Aldrich and used as received. Microanalysis were carried out with a Leco CHNS-932 microanalyser. Conductivities were measured in acetone solution with a Metrohm E 518 conductimeter. IR spectra were recorded with a Nicolet FTIR 740 spectrophotometer in the range 4000–50 cm^{-1} using KBr pellets or nujol mulls. NMR spectra were recorded with an XL-300 Varian spectrometer, ^{1}H and ^{13}C (TMS internal standard) and ^{31}P (H_3PO_4 external standard) spectra were measured from $CDCl_3$ or toluene-d_8 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).

3.1. *trans*-[RhCl(CO)(PCHO)$_2$] (**1**)

To a benzene solution of $[RhCl(CO)_2]_2$ (0.06 mmol) was added an stoichiometric amount (0.24 mmol) of PCHO whereupon evolution of gas is observed and precipitation of a yellow solid occurs which was filtered off, washed with benzene and vacuum-dried. Yield: 45%. IR (cm^{-1}): 1971(s), *v*(C≡O); 1689(s), *v*(C=O); 281(m), *v*(Rh–Cl). ^{1}H-NMR ($CDCl_3$): δ 11.07 (s, CHO). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 187.3 (dt, C≡O), *J*(Rh,C) 73, *J*(P,C) 15; 190.3 (t, CHO), *J*(P,C) 6, *J*(Rh,C) 6. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 28.9 (d), *J*(Rh,P) 127. Anal. Calc. for $C_{39}H_{30}ClO_3P_2Rh$: C, 62.71; H, 4.05. Found: C, 62.59; H, 4.06%.

3.2. [RhH(PCO)Cl(PCHO)] (2)

To a benzene solution of $[RhCl(COD)]_2$ (0.06 mmol) was added an stoichiometric amount (0.24 mmol) of PCHO. Addition of diethyl ether gave a yellow precipitate, which was filtered off, washed with diethyl ether and vacuum-dried. Yield: 68%. IR (cm^{-1}): 2041(m), ν(RhH); 1664(s), 1634(s), ν(C=O); 273(w), ν(Rh–Cl). FABMS: Calc. for $C_{38}H_{30}ClO_2P_2^{103}Rh$: 718; observed: 683 [$M^+$–Cl]. ^{1}H-NMR (toluene-d_8, 223 K): δ −12.98 (ddd, HRh), J(Rh,H) 28, J(P,H) 10, 6; 8.98 (s, CHO). $^{31}P\{^1H\}$-NMR (toluene-d_8): δ 55.3 (dd, PCO), J(Rh,P) 138, J(P,P) 384; 26.2 (dd, PCHO), J(Rh,P) 137. Anal. Calc. for $C_{38}H_{30}ClO_2P_2Rh$: C, 63.48; H, 4.21. Found: C, 63.19; H, 4.22%.

3.3. [RhH(PCO)(Pgdh)]BPh_4 (3)

To an orange benzene solution of $[RhCl(COD)]_2$ (0.04 mmol) was added an stoichiometric amount of PCHO (0.16 mmol) to obtain a yellow solution. Addition of gdh (0.08 mmol) and stirring for 45 min gave a yellow precipitate of [RhH(PCO)(Pgdh)]Cl which was filtered off and dried (75% yield). This solid (0.06 mmol) was dissolved in MeOH and $NaBPh_4$ (0.06 mmol) was added to give a precipitate, which was filtered off, washed with MeOH and vacuum-dried. Yield: 53%. IR (KBr, cm^{-1}): 3485(br), ν(OH); 3429(m), 3281(m), $\nu(NH_2)$; 2049(w), ν(RhH); 1605(s), ν(C=O); 1577(s), ν(C=N). Λ_M (Ω^{-1} cm^2 mol^{-1}): 79 (acetone). FABMS: Calc. for $C_{40}H_{36}N_4O_2P_2^{103}Rh$: 769; observed: 769 [$M^+$] ^{1}H-NMR ($CDCl_3$): δ −13.19 (m, HRh), J(Rh,H) 20, J(P,H) 10; 6.78 (d, HC–N), ^3J(H,H) 10; 5.09 (d, NH); 4.85 (s, NH_2); 2.16 (s, OH); 5.21 (s), 4.76 (s) (HC=N). $^{31}P\{^1H\}$-NMR ($CDCl_2$): δ 60.1 (dd, PCO), J(Rh,P) 126, J(P,P) 304; 25.0 (dd, PNN), J(Rh,P) 120. $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 238.0 (d, CO), J(Rh,C) 31; 141.3 (s), 139.1 (s) (C=N); 84.3 (d, COH), J(P,C) 6. Anal. Calc. for $C_{64}H_{56}BN_4O_2P_2Rh$: C, 70.60; H, 5.18; N, 5.15. Found: C, 70.20; H, 5.32; N, 5.12%.

3.4. [Rh(PCO)(PCHOH)(gdh)]BPh_4 (6)

To a MeOH suspension of $[RhCl(COD)]_2$ (0.12 mmol) were added stoichiometric amounts of gdh (0.24 mmol) and PCHO (0.48 mmol). Stirring for 3h at r.t. gave a yellow precipitate of [Rh(PCO)(PCHOH)-(gdh)]Cl which was filtered and dried (25% yield). 0.05 mmol of this product were dissolved in MeOH, upon addition of $NaBPh_4$ (0.05 mmol) a yellow precipitate was formed, which was filtered off, washed with MeOH and vacuum-dried. IR (KBr, cm^{-1}): 3521(m), ν(OH); 3380(m), 3288(m), 3260(m), $\nu(NH_2)$; 1612(s), ν(C=O); 1577(s), ν(C=N). Λ_M (Ω^{-1} cm^2 mol^{-1}): 116 (acetone). FABMS: Calc. for $C_{40}H_{36}N_4O_2P_2^{103}Rh$: 769; observed: 769 [$M^+$]. ^{1}H-NMR ($CDCl_3$): δ 5.08 (ddd, *H*C–OH), ^3J(H,H) 4, ^2J(Rh,H) 2, ^4J(P,H) 16; 5.91 (s), 5.23 (s) (NH_2); 1.49 (d, OH); 5.99 (s), 5.94 (s) (HC=N). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 55.1 (dd, P_A), J(Rh,P) 132, J(P,P) 316; 45.8 (dd, P_B), J(Rh,P) 130. Anal. Calc. for $C_{64}H_{56}BN_4O_2P_2Rh$: C, 70.60; H, 5.18; N, 5.15. Found: C, 70.23; H, 4.90; N, 5.10%.

3.5. [RhH(PCO)(Ppvdh)]BPh_4 (8)

To a CH_2Cl_2 solution of $[RhCl(COD)]_2$ (0.04 mmol) was added an stoichiometric amount (0.08 mmol) of pvdh whereupon a red precipitate was formed that upon addition of PCHO (0.16 mmol) gave a yellow solution from which a yellow precipitate of [RhH-(PCO)(Ppvdh)]Cl appear which was filtered off and dried (50% yield). To a MeOH solution of [RhH-(PCO)(Ppvdh)]Cl (0.06 mmol) was added $NaBPh_4$ (0.06 mmol) to give a precipitate which was filtered off, washed with MeOH and vacuum-dried. Yield: 70%. IR (KBr, cm^{-1}): 3525(br), ν(OH); 3387(m), 3302(w), 3225(w) $\nu(NH_2)$; 2048(w), ν(RhH); 1612(s), ν(C=O); 1576(s), ν(C=N). Λ_M (Ω^{-1} cm^2 mol^{-1}): 96 (acetone). FABMS: Calc. for $C_{41}H_{38}N_4O_2P_2^{103}Rh$: 783; observed: 783 [$M^+$]. ^{1}H-NMR ($CDCl_3$): δ −13.24 (m, HRh), J(Rh,H) 20, J(P,H) 10; 5.07 (d, NH), ^3J(H,H) 9; 4.92 (s, NH_2); 5.46 (s) (HC=N); 0.94 (s, CH_3) for **8a**; −13.02 (m, HRh), J(Rh,H) 20, J(P,H) 10; 5.25 (d, NH), ^3J(H,H) 9; 4.47 (s, NH_2); 2.07 (s, OH); 4.86 (s) (HC=N); 0.84 (s, CH_3) for **8b**. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 61.5 (dd, PCO), J(Rh,P) 128, J(P,P) 309; 25.1 (dd, PNN), J(Rh,P) 121 for **8a**; 60.0 (dd, PCO), J(Rh,P) 126, J(P,P) 307; 26.1 (dd, PNN), J(Rh,P) 119 for **8b**. Anal. Calc. for $C_{65}H_{58}BN_4O_2P_2Rh$: C, 70.79; H, 5.30; N, 5.08. Found: C, 70.37; H, 5.56; N, 4.83%.

Acknowledgements

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