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New Acylhydrido- and Diacylrhodium(III) Organocomplexes Derived from 8-Quinolinecarbaldehyde and/or *o*-(Diphenylphosphanyl)benzaldehyde

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The acylhydridorhodium(III) complex [RhHCl{PPh_2(*o*-C_6H_4-CO)}(py)$_2$] (**1**) reacts with 8-quinolinecarbaldehyde (C_9H_6NCHO) to afford mixed diacyl [RhCl(C_9H_6NCO)-{PPh_2(*o*-C_6H_4CO)}(py)] (**2**) with acyl groups *trans* to chlorine and to pyridine. Complex **1** undergoes displacement of pyridine by 2-(aminomethyl)pyridine (ampy) or diphosphanes to give hydridoacyl neutral [RhHCl{PPh_2(*o*-C_6H_4CO)}(LL)] [LL = ampy (**3**), bis(diphenylphosphanyl)methane (dppm, **5**), 1,3-bis(diphenylphosphanyl)propane (dppp, **6**), 1,2-bis(diphenylphosphanyl)ethane (dppe, **7**)] with hydride *trans* to chloride. Complex **3** exchanges hydride with chloride to give [Rh(Cl)$_2$-{PPh_2(*o*-C_6H_4CO)}(ampy)] (**4**). The reaction of **2** with bidentate N-donor ligands yields cationic mixed diacyl [Rh(C_9H_6NCO){PPh_2(*o*-C_6H_4CO)}(NN)]$^+$ species [NN = 2,2′-bipyridine (bipy, **8**), ampy (**9**)]. Neutral or cationic diacyl complexes that contain two acylquinoline fragments can be obtained by the reaction of dimer [Rh(μ-Cl)(C_9H_6NCO)$_2$]$_2$ (**10**) with pyridine to give [Rh(Cl)(C_9H_6NCO)$_2$(py)] (**11**) or with bidentate N- or P-donor ligands (LL) to afford [Rh(C_9H_6NCO)$_2$-(LL)]$^+$ [LL = dppm (**12**), dppe (**13**), dppp (**14**), 1,4-bis(diphenylphosphanyl)butane (**15**), ampy (**16**), 8-aminoquinoline (**17**), biacetyldihydrazone (**18**), bipy (**19**)] with the acyl groups *trans* to LL. Complex **11** is highly fluxional in solution. At low temperatures, the acylquinoline chelate opens to allow an intramolecular exchange between **11a** and **11b** ($\Delta H^{\ddagger}$ = 10.1 ± 0.2 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 1.0 ± 0.1 cal K^{-1} mol^{-1}), and pyridine dissociation occurs at room temperature. All the complexes were characterized spectroscopically. Single crystal X-ray diffraction analysis was performed on **2**.

Introduction

Organometallic rhodium complexes that contain phosphorus ligands play an important role in the transformation of many organic compounds.[1] More recently, nitrogen ligands have been more widely used in the design of regio- and/or enantioselective catalytic systems.[2] The transfer hydrogenation of C=O bonds with 2-propanol as a source of hydrogen is an attractive method for the preparation of secondary alcohols by avoiding the use of molecular hydrogen and pressure apparatus.[3] Metal hydrides, often prepared in situ, may catalyze the transfer hydrogenation of ketones.[4] Complexes that contain N- and P-donor ligands, such as 2-(aminomethyl)pyridine phosphane ruthenium(II) complexes, are among the most active catalysts for this reaction.[5] Iridium complexes that contain an acylphosphane chelate and an acylquinoline chelate have been found to be more useful for the transfer hydrogenation reaction than analogous complexes that contain only acylphosphane groups. In alcoholic media and in the presence of strong bases, iridium acyls can afford iridium acylhydrides.[6] Acylhydrido metal complexes can be easily prepared by the oxidative addition of aldehydes to low-valent transition metal complexes.[7] We have reported that *o*-(diphenylphosphanyl)benzaldehyde reacts with rhodium(I) complexes to afford saturated acylhydridorhodium(III) derivatives such as [RhHCl{PPh_2(*o*-C_6H_4CO)}(py)$_2$] or [RhHCl{PPh_2(*o*-C_6H_4CO)}{κ^1-PPh_2(*o*-C_6H_4CHO)}(py)]. The latter contains an uncoordinated aldehyde and may afford acylhydroxyalkyl [RhCl{PPh_2(*o*-C_6H_4CO)}{PPh_2(*o*-C_6H_4-CHOH)}(py)] complexes by migration of hydride or diacyl [RhCl{PPh_2(*o*-C_6H_4CO)}$_2$(py)] derivatives by hydrogen loss.[8] Cationic diacyl complexes [Rh{PPh_2(*o*-C_6H_4CO)}$_2$(NN)]$^+$ have also been obtained by displacement reactions of pyridine and chloride with N-donor bidentate ligands (NN).[9] 8-Quinolinecarbaldehyde allows the chelate-assisted oxidative addition of the aldehyde to rhodium(I) derivatives to produce stable saturated and unsaturated rhodium(III) acylhydrides and has also been reported to promote the loss of H_2.[10]

We report the reactivity of the acylhydridorhodium(III) complex [RhHCl{PPh_2(*o*-C_6H_4CO)}(py)$_2$] (**1**) with 8-quinolinecarbaldehyde or with bidentate N- or P-donor ligands

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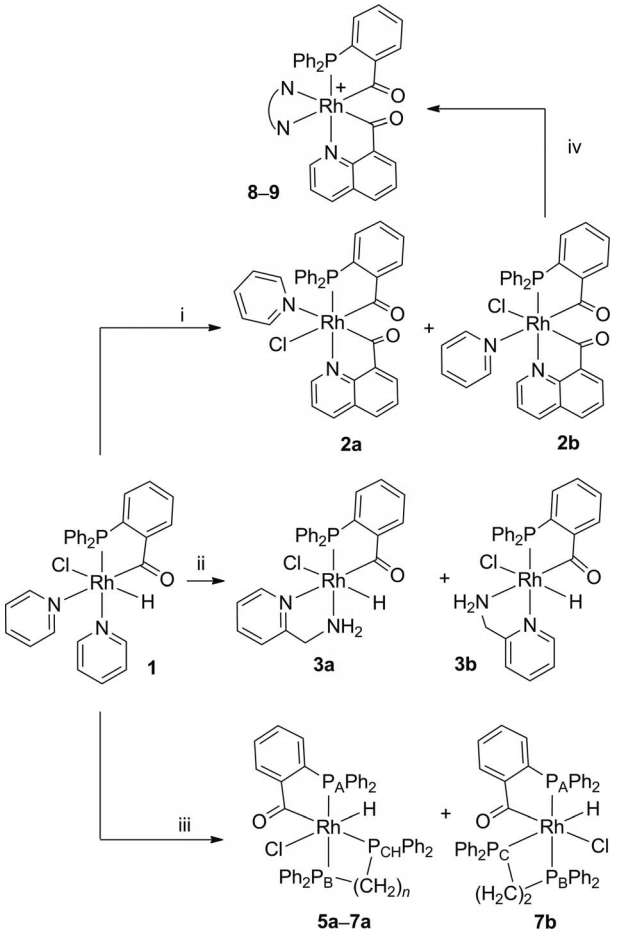
to afford neutral, mixed diacyl- or acylhydridorhodium(III) complexes, respectively. Neutral and cationic diacyl complexes derived from 8-quinolinecarbaldehyde are also reported. The catalytic activity of acylhydrido- and of diacylrhodium(III) complexes in the transfer hydrogenation of cyclohexanone has been studied.

Results and Discussion

The reaction of **1** with 8-quinolinecarbaldehyde led to $[RhCl(C_9H_6NCO)\{PPh_2(o\text{-}C_6H_4CO)\}(py)]$ (**2**) as a mixture of two diacyl complexes **2a** and **2b** in a **2a**/**2b** ratio of 6:1, which was shown by the $^{31}P\{^1H\}$ NMR spectrum. The appearance of two close doublets at 69.6 and 64.5 ppm with J(Rh,P) values of 188 and 177 Hz, respectively, suggests that in both complexes the phosphorus atom is *trans* to an electronegative group. This mixture remains unchanged in the 298–233 K range. In the $^{13}C\{^1H\}$ NMR spectrum, only a broad doublet due to the acyl groups bonded to rhodium is observed at 225 ppm. The separation of **2a** and **2b** was unsuccessful. The spectroscopic features and the X-ray diffraction of **2a** led us to propose the structures for **2a** and **2b** shown in Scheme 1 (see i). In related diacylrhodium $[RhCl\{PPh_2(o\text{-}C_6H_4CO)\}_2(L)]$ complexes that contain different pyridine ligands (L), the acyl groups are *trans* to chlorine and pyridine.[8,9a]



Scheme 1. i) C_9H_6N–CHO. ii) 2-(aminomethyl)pyridine (ampy). iii) PP = bis(diphenylphosphanyl)methane (dppm, **5**), 1,3-bis(diphenylphosphanyl)propane (dppp, **6**), 1,2-bis(diphenylphosphanyl)ethane (dppe, **7**). iv) NN = 2,2′-bipyridine (bipy, **8**), ampy (**9**).

The X-ray diffraction study of **2a** confirmed the proposed structure. This compound crystallized in the $P2_1/n$ monoclinic space group, and the crystal consisted of a neutral Rh compound and a dichloromethane solvent molecule. The molecular structure of **2a** is shown in Figure 1. The geometry around the metal atom is distorted octahedral with four positions occupied by the two bidentate ligands and the other two positions occupied by the pyridine and the chloride ligands, *trans* to C20 and C1 of the acylquinoline and acylphosphane fragments, respectively. The distances that comprise the chelate rings are in the expected ranges.[9a,11,12] The Rh1–N2 distance with N2 *trans* to acyl is 0.15(1) Å longer than the Rh1–N1 distance with N1 *trans* to phosphorus. These distances agree with the *trans* influence order of the ligands: acyl > phosphane.[13] The rhodium atom is practically included in the acylquinoline ligand plane, whereas the acylphosphane chelate ring forms a dihedral angle of 19.97(2)° between the C1–Rh1–P1 plane and the corresponding phenyl ring.

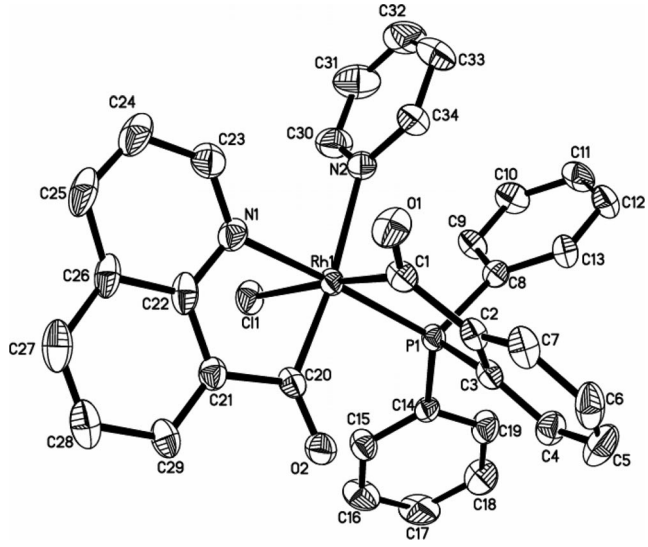


Figure 1. ORTEP view of **2a**, which shows the atomic numbering (20% probability ellipsoids). The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1–C1 2.01(1), Rh1–C20 1.979(9), Rh1–P1 2.259(2), Rh1–N1 2.12(1), Rh1–N2 2.27(1), Rh1–Cl1 2.507(3), C1–O1 1.21(1), C20–O2 1.23(1), Cl1–Rh1–C1 175.5(3), Cl1–Rh1–C20 89.0(3), C20–Rh1–N1 82.9(4), C20–Rh1–C1 86.5(4), C20–Rh1–P1 91.9(3), C20–Rh1–N2 173.3(3), N1–Rh1–P1 172.6(2).

The reaction shown in Scheme 1 (i) formally involves aldehyde C–H bond activation and hydrogen evolution. Aldehyde activation by complexes of metals in higher oxidation states has been proposed to occur mainly by oxidative addition or σ-bond metathesis.[7i] The former appears less likely in our case because it would involve scarce Rh^V intermediates.[14] The σ-bond metathesis, or a related σ complex-assisted metathesis mechanism,[15] is more feasible. We have

observed that the acylnorbornenylrhodium(III) complex [RhCl(C_9H_6NCO)(norbornenyl)(κ^2-C_9H_6NCHO)], which contains a coordinated κ^2-*N*,*O*-aldehydequinoline, undergoes H transfer from the coordinated aldehyde to the σ-norbornenyl group to release norbornene.[12] Therefore, we believe that the reaction shown in Scheme 1 (i) occurs by aldehyde–quinoline displacement of pyridine from **1**, H transfer from the coordinated C_9H_6NCHO to the hydride and H_2 release.

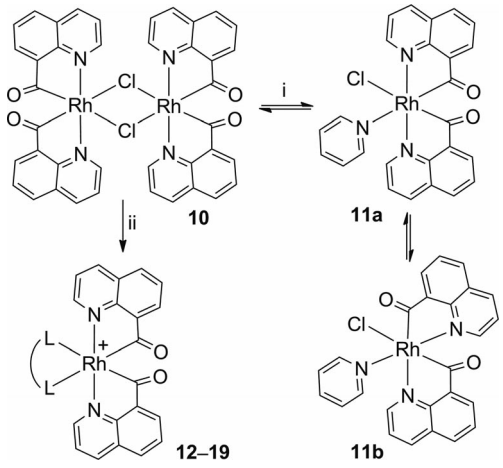
The reaction of **1** with 2-(aminomethyl)pyridine (= ampy; Scheme 1, ii) shows the easy displacement of pyridine by chelating ligands, which led to the formation of neutral acylhydridorhodium(III) [RhHCl{PPh_2(*o*-C_6H_4CO)}(ampy)] (**3**), which contains an acylphosphane fragment and a bidentate N-donor ligand. The NMR spectra show that **3** is a mixture of two isomers **3a** and **3b** in a 3:1 ratio. The $^{31}P\{^1H\}$ NMR spectrum contains two doublets in the 73.1–73.5 ppm range with *J*(Rh,P) of 163 Hz, and the ^1H NMR spectrum shows two triplets in the high field region at –16.45 and –15.07 ppm, which are consistent with hydrides *cis* to phosphorus [*J*(P,H) = *J*(Rh,H) = 25 Hz] and *trans* to chloride. The resonances due to the amino groups at 4.95 and 4.23 ppm for the more abundant **3a** and at 2.77 and 2.23 ppm for **3b** indicate different environments for the amino groups in both isomers. In the absence of other effects, the corresponding signals are expected to shift downfield upon coordination, but the ring current effects originated by the aromatic rings of the phosphane can shift the signals upfield.[16] Therefore, we assign the two resonances at lower field, 4–5 ppm, to the isomer that contains the amino group *trans* to phosphorus, **3a**, and the signals at higher field, 2–3 ppm, to the isomer that contains the amino group *cis* to phosphorus, **3b**. In solution, **3** showed low stability, which precluded the separation of the isomers. In chlorinated solvents, the exchange of hydride by chloride afforded [$RhCl_2${PPh_2(*o*-C_6H_4CO)}(ampy)] (**4**) as a mixture of two isomers **4a** and **4b** in a 4:1 ratio. When performing the reaction in $CDCl_3$, the appearance of a resonance at 5.30 ppm in the ^1H NMR spectrum due to formation of dichloromethane was observed. Such a reaction has several precedents.[8,17]

The reaction of **1** with diphosphanes afforded the acylhydrides [RhHCl{PPh_2(*o*-C_6H_4CO)}{$Ph_2P(CH_2)_nPPh_2$}] (**5**–**7**, Scheme 1, iii). With bis(diphenylphosphanyl)methane (dppm) and 1,3-bis(diphenylphosphanyl)propane (dppp), single isomers **5a** and **6a** were obtained, respectively, which contain the hydride *trans* to chloride, and were unambiguously characterized by NMR spectroscopy. The ^1H NMR spectra show multiplets in the high field region at –13.92 (**5a**) or –18.91 ppm (**6a**) due to rhodium-coordinated hydrides *cis* to three phosphorus atoms [*J*(Rh,H) = 26.3 or 24.3 Hz; *J*(P,H) = 12.6 or 12.8, 9.0 or 10.7 and 5.3 Hz or unobserved]. The $^{31}P\{^1H\}$ NMR spectra contain resonances at 61.0 (ddd) (**5a**) or 51.6 (ddd) ppm (**6a**) due to P_A coordinated to rhodium [*J*(Rh,P_A) = 128 or 119 Hz] *trans* to P_B [*J*(P_B,P_A) = 374 or 335 Hz] and *cis* to P_C [*J*(P_C,P_A) = 23 or 27 Hz]; –7.0 (dd) (**5a**) or 14.5 (ddd) (**6a**) ppm due to P_B [*J*(Rh,P_B) = 114 or 121 Hz] *cis* to P_C [*J*(P_C,P_B) = unobservable or 46 Hz] and –18.2 (dd) (**5a**) or 0.7 (ddd) (**6a**) ppm due to P_C *trans* to the acyl group [*J*(Rh,P_C) = 54 or 69 Hz]. The $^{13}C\{^1H\}$ NMR spectra contain the expected resonances due to an acyl group coordinated to rhodium at 239.1 (dd) (**5a**) or 241.9 (dd) (**6a**) ppm [*J*(Rh,C) = 28 Hz] and *trans* to phosphorus [*J*(P,C) = 122 or 141 Hz].

The reaction of **1** with 1,2-bis(diphenylphosphanyl)ethane (dppe) gave a 1:1 mixture of two isomers **7a** and **7b**. The NMR spectra allow the unambiguous characterization of both complexes that differ in the group *trans* to the most electronegative chloride, which is hydride in **7a** and acyl in **7b**. Complex **7a** contains a hydride (–15.32 ppm) bonded to rhodium [*J*(Rh,H) = 25.3 Hz], which is *cis* to three phosphorus atoms [*J*(P,H) = 12.1, 12.0 and 6.5 Hz], whose resonances in the $^{31}P\{^1H\}$ NMR spectrum are similar to those of **6a** and appear at 59.8 (ddd), 50.6 (ddd) and 33.5 (ddd) ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance of the acyl group at 244.7 (dd) ppm *trans* to phosphorus [*J*(P,C) = 120 Hz] is observed. Complex **7b** contains a hydride (–7.46 ppm) bonded to rhodium [*J*(Rh,H) = 18.2 Hz], which is *trans* to phosphorus [*J*(P,H) = 161.8 Hz] and *cis* to the other two phosphorus atoms [$J(P,H)_{cis}$ = unobservable and 8.9 Hz]. The $^{31}P\{^1H\}$ NMR spectrum contains the expected splitting pattern for the resonances at 65.8 (ddd), 58.6 (ddd) and 28.5 (ddd) ppm due to **7b** and the $^{13}C\{^1H\}$ NMR spectrum shows the expected doublet of the acyl group at 232.2 ppm due to rhodium coupling [*J*(Rh,C) = 32 Hz]. Attempts to separate the isomers led to decomposition. The reaction of **1** with 1,4-bis(diphenylphosphanyl)-butane (dppb) led to a complex mixture of compounds, which included compounds of the type **7a** and **7b** along with other unidentified species.

Complex **2** reacted with bidentate N-donor ligands (NN) such as 2,2′-bipyridine (bipy) or 2-(aminomethyl)pyridine to undergo displacement of pyridine and chloride and afford cationic, mixed diacyl [Rh(C_9H_6NCO){PPh_2(*o*-C_6H_4CO)}(NN)]$^+$ derivatives [NN = bipy (**8**), ampy (**9**)], which were isolated as tetraphenylborate compounds (Scheme 1, iv) and behave as 1:1 electrolytes.[18] Their $^{31}P\{^1H\}$ NMR spectra contain one doublet in the 65.2–63.6 ppm range with *J*(Rh,P) values from 179–166 Hz, which is consistent with phosphorus lying *trans* to nitrogen. The $^{13}C\{^1H\}$ NMR spectra show two doublets in the low field region due to acyl groups bonded to rhodium and *cis* to a phosphorus atom at 235.0 [*J*(Rh,C) = 31 Hz] and 229.0 [*J*(Rh,C) = 37 Hz] ppm for **8** or at 237.0 [*J*(Rh,C) = 31 Hz] and 233.2 [*J*(Rh,C) = 37 Hz] ppm for **9**. For complex **8**, the formation of only one species is observed. Its ^1H NMR spectrum shows resonances due to the amino group at 3.79 and 2.37 ppm. All these data suggest the structure depicted in Scheme 1 (iv), in which the phosphorus atom lies *trans* to the quinolinic N-atom and the acyl groups lie *trans* to the bidentate N-donor ligand. On spectroscopic grounds alone it is not possible to determine whether the amino group of ampy is *trans* to the acyl group of the acylquinoline or the acylphosphane. Unfortunately, repeated attempts to obtain single crystals suitable for X-ray diffraction were unsuccessful.

Neutral or cationic diacyl complexes that contain two acylquinoline fragments were obtained by the reaction of dimeric $[Rh(\mu\text{-}Cl)(C_9H_6NCO)_2]_2$ (**10**)[12] with pyridine or bidentate N- or P-donor ligands, respectively (Scheme 2).



Scheme 2. i) pyridine. ii) LL = dppm (**12**), dppe (**13**), dppp (**14**), dppb (**15**), ampy (**16**), 8-aminoquinoline (aqui, **17**), biacetyldihydrazone (bdh, **18**), bipy (**19**).

The reaction of **10** with pyridine (Scheme 2, i) led to the cleavage of the chlorine bridge to afford neutral $[Rh(Cl)(C_9H_6NCO)_2(py)]$ (**11**), which was highly fluxional in solution and underwent two different fluxional processes: i) exchange between **11a** and **11b** at low temperatures and ii) pyridine dissociation at room temperature. As shown in Figure 2, at 183 K three resonances are observed in the low field region of the ^{1}H NMR spectrum at δ = 10.10, 9.41 and 8.64 ppm. We attribute the low field resonance to H2 of the coordinated 8-acylquinoline group. Deshielding of this signal with respect to free C_9H_6NCHO has been observed in neutral (acylquinoline)palladium complexes.[19] The resonances at 9.41 and 8.64 ppm are attributed to H2 of the coordinated pyridine ring, which is present in **11a** and **11b** (Scheme 2, i). Although other geometries cannot be excluded, our proposal is based on the structure of **2** and the observed tendency of acylquinoline derivatives to locate the acyl group *trans* to chloride and the nitrogen atom *trans* to another nitrogen atom when available.[12,19] A temperature increase led to the broadening of the resonances at 9.41 and 8.64 ppm, followed by coalescence at 233 K with the emergence of a new signal at δ = 9.11 ppm, which became sharp at 253 K. In the 183–253 K range the resonance at 10.10 ppm is clearly observed. From line-shape analysis (Figure 3) of the variable temperature ^{1}H NMR spectra in the 183–253 K range,[20] the activation parameters $\Delta H^{\ddagger}$ = 10.1 ± 0.2 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 1.0 ± 0.1 cal K^{-1} mol^{-1} were determined. The relatively small value of the entropy of activation falls in the range between 11 and –10 cal K^{-1} mol^{-1}, which could be indicative of an intramolecular rearrangement processes.[21] Fast exchange between **11a** and **11b** by the opening of the acylquinoline chelate could explain the fluxional behaviour. As shown in Figure 2, at temperatures higher than 263 K, the broadening and collapse of the reso-

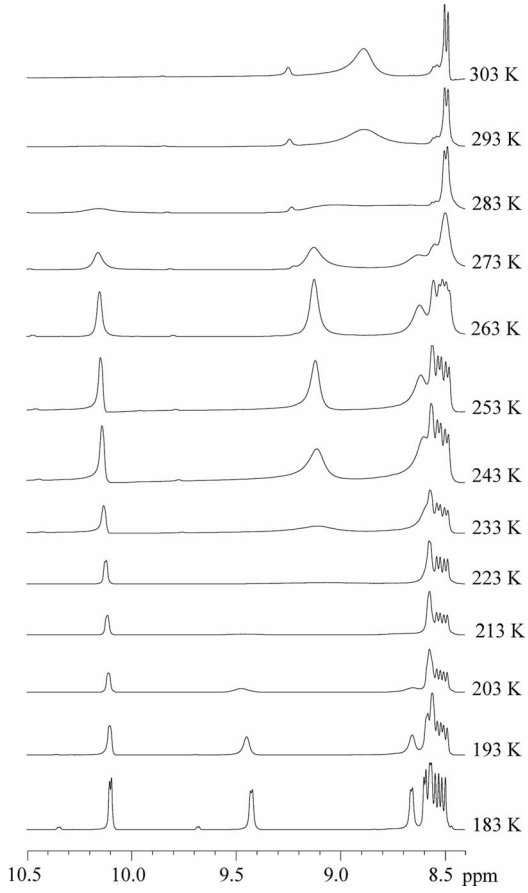


Figure 2. Variable-temperature ^{1}H NMR spectra of **11** in CD_2Cl_2 from 183–303 K.

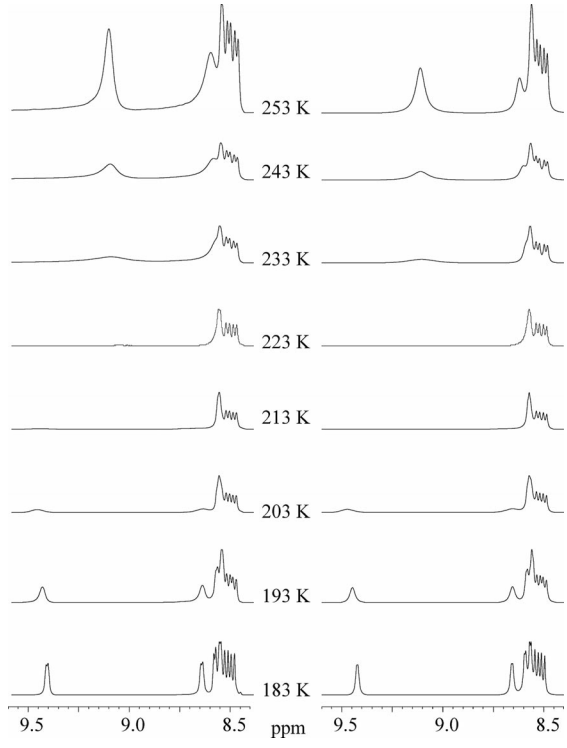


Figure 3. Variable-temperature ^{1}H NMR spectra of **11** in CD_2Cl_2 from 183–263 K: (left) experimental and (right) calculated.

nances at 9.11 and 10.10 ppm occurred, which indicates the dissociation of pyridine and the presence of a mixture of **10** and free pyridine at room temperature and above. Repeated attempts to obtain single crystals of **11** suitable for X-ray diffraction were unsuccessful.

The reaction of **10** with different bidentate ligands (LL), such as diphosphanes $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 3 or 4), N-donor ligands of the aminoimino type (aqui or ampy) or with aromatic (bipy) or aliphatic (bdh) diimines, afforded cationic diacyl $[Rh(C_9H_6NCO)_2(LL)]^+$ derivatives (**12**–**19**, Scheme 2, ii), which were isolated as tetraphenylborate compounds. The complexes show the expected features in their IR spectra and behave as 1:1 electrolytes in acetone solution. In the $^{31}P\{^1H\}$ NMR spectra of **12**–**15** only one doublet is observed with J(Rh,P) in the 63–72 Hz range, which is consistent with equivalent phosphorus atoms being *trans* to acyl groups.[22] The chemical shifts and their displacement upon coordination (ΔF) are as expected for complexes that contain four- [dppm, –16.2 (ΔF = +5) ppm], five- [dppe, +27.9 (ΔF = +35) ppm], six- [dppp, –6.9 (ΔF = +10) ppm] or seven-membered [dppb, –2.3 (ΔF = +12) ppm] metallacycles.[23] Accordingly, the $^{13}C\{^1H\}$ NMR spectrum of **13** shows a doublet of doublets at low field (232.3 ppm) due to equivalent acyl groups bonded to rhodium [J(Rh,C) = 27 Hz] and *trans* to phosphorus atoms [J(P,C) = 95 Hz]. Complexes **16**–**19**, which contain N-donor ligands adopt an analogous geometry. The $^{13}C\{^1H\}$ NMR spectra of **16**–**17**, which contain asymmetric ligands, show two doublets in the 235–226 ppm range due to nonequivalent rhodium-bonded acyl groups [J(Rh,C) = 33 Hz]. For **18**–**19**, which contain symmetric ligands, only one doublet in the 231–229 ppm range due to equivalent rhodium-bonded acyl groups [J(Rh,C) = 33 Hz] is observed. The ^1H NMR spectrum of **18**, which contains biacetyldihydrazone $[H_2NN{=}C(CH_3)C(CH_3){=}NH_2]$, confirms the presence of two equivalent imino fragments.

Complexes **2**, **8** and **9** contain the best σ-donor acyl groups *trans* to more electronegative atoms such as chlorine or nitrogen and phosphorus atoms *trans* to nitrogen as expected when electronic effects are taken into consideration. In contrast, in **12**–**15** the nitrogen atoms are mutually *trans* and the acyl groups are *trans* to the phosphorus atoms. We believe that **12**–**15** are the kinetically favoured products of the reaction of the diphosphanes with **10**, which contains mutually *trans* N-atoms and bridging chlorides. This behaviour has also been observed in the formation of triscyclometallated homoleptic $(C,N)_3$ iridium(III) complexes, where the isomerization of the kinetic *mer* isomer to the thermodynamically favoured *fac* isomer requires reaction temperatures higher than 200 °C or a photochemical reaction.[24]

The use of acyl complexes in the transfer hydrogenation of ketones with alcohols has been limited to a few iridium complexes.[6b,25] We have studied the catalytic activity of hydridoacyl complexes **1**, **3**, **5**–**7**, diacyl complexes **2** and **10** and related $[RhCl\{PPh_2(o\text{-}C_6H_4CO)\}_2(py)]$ (**20**),[8] which contains two acylphosphane chelates, in the hydrogen transfer from 2-propanol to cyclohexanone in *i*PrOH in the presence of a strong base. From the transfer hydrogenation data it is apparent that **1** reaches 70% conversion to cyclohexanol after 180 min [turnover frequency (TOF) = 202]. As shown in Table 1, **3**, which contains 2-(aminomethyl)pyridine, and **6** and **7**, which contain dppp and dppe, respectively, show a higher catalytic activity, and reach over 80% conversion in 60 min. The presence of two chelates in these complexes markedly enhances their catalytic properties, which has been observed in bis(chelated) Rh^{III} bis(carbene) complexes.[26] The catalytic activity of **6** and **7** is comparable to that reported for chelated or pincer Rh^{III} carbene complexes[27] and higher than that shown by related acyliridium complexes.[6b,25] The presence of dppm in **5** inhibits the catalytic activity. The diacyl complexes show lower catalytic activity than the hydridoacyl derivatives. Complex **20**, which contains two acylphosphane chelates, required 180 min to reach 80% conversion (TOF = 360). The substitution of acylphosphane chelates by acylquinoline chelates resulted in a decrease in the catalytic activity. The mixed compound **2** reached only 66% conversion after 180 min (TOF = 360) due to fast catalyst deactivation, and **10**, which contains two acylquinoline chelates, gave only 18% conversion, or 24% conversion in the presence of pyridine, after 180 min.

Table 1. Transfer hydrogenation of cyclohexanone with hydridoacyl complexes.[a]

Complex	Conversion [%][b]	TOF[c]
1	50/59	202
3	80/92	324
5	65/76	68
6	90/96	415
7	88/93	381

[a] Reaction conditions: 0.1 M substrate in *i*PrOH (40 cm^3) with 0.5 mol-% precatalyst loading at 83 °C. [KOH]/[Rh] 10:1. [b] Reaction time: 60/90 min. [c] Calculated after 10 min and expressed in mol of product/(mol of complex × h).

Conclusions

The reaction between $[RhHCl\{PPh_2(o\text{-}C_6H_4CO)\}(py)_2]$ and C_9H_6NCHO to afford mixed diacyl $[RhCl(C_9H_6NCO)\{PPh_2(o\text{-}C_6H_4CO)\}(py)]$ may occur by quinolinealdehyde coordination, followed by H transfer from coordinated aldehyde to hydride to release H_2. Neutral hydridoacyl compounds, with hydride *trans* to chloride, and cationic diacyl complexes, with acyl groups *trans* to phosphorus or nitrogen, were easily formed by the reaction with bidentate P- or N-donor ligands. Hydridoacyl complexes catalyze the hydrogen transfer from 2-propanol to cyclohexanone to afford cyclohexanol.

Experimental Section

General Procedures: The preparation of the metal complexes was carried out at room temperature under nitrogen with the use of standard Schlenk techniques. $[RhClH\{PPh_2(o\text{-}C_6H_4CO)\}(py)_2]$[8] (**1**), $[RhCl\{PPh_2(o\text{-}C_6H_4CO)\}_2(py)]$[8] (**20**), $[Rh(\mu\text{-}Cl)(C_9H_6NCO)_2]_2$[12] (**10**) and 8-quinolinecarbaldehyde[19] were prepared as

previously reported. Microanalysis was 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 including 2D experiments were recorded with Bruker Avance DPX 300 or Bruker Avance 500 spectrometers, ^1H and $^{13}C\{^1H\}$ (Me_4Si internal standard) and $^{31}P\{^1H\}$ NMR (H_3PO_4 external standard) spectra were measured from $CDCl_3$ or CD_2Cl_2 solutions.

[RhCl(C_9H_6NCO){PPh_2(*o*-C_6H_4CO)}(py)] (2): To a methanol suspension of [RhClH{PPh_2(*o*-C_6H_4CO)}$(py)_2$] (**1**) (180 mg, 0.307 mmol) was added 8-quinolinecarbaldehyde (48 mg, 0.307 mmol). The suspension was stirred at room temperature for 3 h. The solid was collected by filtration, washed with methanol and dried under vacuum; yield 100 mg, 49%. IR (KBr): $\tilde{\nu}$ = 1660 (m), 1626 [s, ν(C=O)] cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 69.6 [d, J(Rh,P) = 188 Hz, P_{2a}], 64.5 [d, J(Rh,P) = 177 Hz, P_{2b}] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 225.0 [d, J(Rh,C) = 35 Hz, *C*O] ppm. $C_{34}H_{25}ClN_2O_2PRh{\cdot}CH_3OH$ (694.96): calcd. C 60.49, H 4.21, N 4.03; found C 60.13, H 3.82, N 4.12.

[RhHCl{PPh_2(*o*-C_6H_4CO)}(ampy)] (3): To a benzene suspension of **1** (75 mg, 0.128 mmol) was added 2-(aminomethyl)pyridine (13.3 µL, 0.128 mmol). After stirring for 1 h, the colour of the suspension changed to afford a white solid, which was collected by filtration, washed with benzene and dried under vacuum; yield 51 mg, 75%. IR (KBr): $\tilde{\nu}$ = 3272 (m), 3230 [m, ν(NH_2)], 2065 [m, ν(Rh–H)], 1602 [s, ν(C=O)] cm^{-1}. **Data for 3a**: ^1H NMR (CD_2Cl_2): δ = 4.95 (m, 1 H, NH_2), 4.76 (m, 1 H, CH_2), 4.46 (m, 1 H, CH_2), 4.23 (br., 1 H, NH_2), –16.45 [t, J(Rh,H) = J(P,H) = 25.0 Hz, 1 H, RhH] ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 73.1 [d, J(Rh,P) = 163 Hz] ppm. **Data for 3b**: ^1H NMR (CD_2Cl_2): δ = 4.71 (m, 1 H, CH_2), 4.41 (m, 1 H, CH_2), 2.77 (br., 1 H, NH_2), 2.23 (br., 1 H, NH_2), –15.07 [t, J(Rh,H) = J(P,H) = 25.7 Hz, 1 H, RhH] ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 73.5 [d, J(Rh,P) = 164 Hz] ppm. $C_{25}H_{23}ClN_2OPRh$ (536.80): calcd. C 55.94, H 4.32, N 5.22; found C 55.68, H 4.34, N 5.44.

[$Rh(Cl)_2${PPh_2(*o*-C_6H_4CO)}(ampy)] (4): Stirring a dichloromethane solution of **3** (50 mg, 0.093 mmol) for 18 h afforded an orange solution. Addition of diethyl ether gave a yellow solid, which was collected by filtration, washed with diethyl ether and dried under vacuum; yield 28 mg, 53%. IR (KBr): $\tilde{\nu}$ = 3314 (w), 3272 (w), 1652 [s, ν(C=O)]. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 13 (acetone). **Data for 4a**: ^1H NMR ($CDCl_3$): δ = 5.40 (br., 1 H, CH_2), 4.83 (br., 1 H, NH_2), 4.73 (br., 1 H, NH_2), 4.64 (br., 1 H, CH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 55.7 [d, J(Rh,P) = 139 Hz] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 229.8 [d, J(Rh,C) = 27 Hz, *C*O], 51.3 (s, CH_2) ppm. **Data for 4b**: ^1H NMR ($CDCl_3$): δ = 4.64 (br., 1 H, CH_2), 4.43 (br., 1 H, CH_2), 4.29 (br., 1 H, NH_2), 4.12 (br., 1 H, NH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 56.4 [d, J(Rh,P) = 137 Hz] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 229.0 [d, J(Rh,C) = 24 Hz, *C*O], 48.2 (s, CH_2) ppm. $C_{25}H_{22}Cl_2N_2OPRh{\cdot}0.5CH_2Cl_2$ (613.72): calcd. C 49.91, H 3.78, N 4.57; found C 49.63, H 3.76, N 5.09.

[RhHCl{PPh_2(*o*-C_6H_4CO)}(PP)] [PP = dppm (5a), dppp (6a), dppe (7)]: To a benzene solution of the corresponding ligand (0.119 mmol) (room temperature for **5a** and **7** or 40 °C for **6a**) was added **1** (70 mg, 0.119 mmol) to afford a yellow solution. After stirring for 15 min, hexane was added to afford a yellow precipitate, which was collected by filtration, washed with hexane and dried under vacuum. **Data for 5a**: Yield 78 mg, 80%. IR (KBr): $\tilde{\nu}$ = 2051 [m, ν(Rh–H)], 1623 [s, ν(C=O)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = –13.92 [m, J(Rh,H) = 26.3, J(P,H) = 12.6, 9.0 and 5.3 Hz, 1 H, RhH] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 61.0 [ddd, J(Rh,P_A) = 128, J(P_B,P_A) = 374, J(P_C,P_A) = 23 Hz, P_A], –6.95 [dd, J(Rh,P_B) = 114 Hz, P_B], –18.20 [dd, J(Rh,P_C) = 54 Hz, P_C] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 239.1 [dd, J(P,C) = 122, J(Rh,C) = 28 Hz, *C*O] ppm. $C_{44}H_{36}ClOP_3Rh$ (813.06): calcd. C 65.00, H 4.59; found C 65.40, H 5.23. **Data for 6a**: Yield 73 mg, 73%. IR (KBr): $\tilde{\nu}$ = 2107 [m, ν(Rh–H)], 1616 [s, ν(C=O)] cm^{-1}. ^1H NMR (CD_2Cl_2): δ = –18.91 [m, J(Rh,H) = 24.3, J(P,H) = 12.8 and 10.7 Hz, 1 H, RhH] ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 51.6 [ddd, J(Rh,P_A) = 119, J(P_B,P_A) = 335, J(P_C,P_A) = 27 Hz, P_A], 14.5 [ddd, J(Rh,P_B) = 121, J(P_C,P_B) = 46 Hz, P_B], 0.7 [ddd, J(Rh,P_C) = 69 Hz, P_C] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 241.9 [dd, J(P,C) = 141, J(Rh,C) = 29 Hz, *C*O] ppm. $C_{46}H_{40}ClOP_3Rh$ (841.12): calcd. C 65.69, H 4.91; found C 65.34, H 5.07. **Data for 7**: Yield 58 mg, 59%. IR (KBr): $\tilde{\nu}$ = 1939 [m, ν(Rh–H)], 1622 [s, ν(C=O)] cm^{-1}. **Data for 7a**: ^1H NMR ($CDCl_3$): δ = –15.32 [m, J(Rh,H) = 25.3, J(P,H) = 12.1, 12.0 and 6.5 Hz, 1 H, RhH] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 59.8 [ddd, J(Rh,P_A) = 121, J(P_B,P_A) = 356, J(P_C,P_A) = 19 Hz, P_A], 50.6 [ddd, J(Rh,P_B) = 120, J(P_C,P_B) = 13 Hz, P_B], 33.5 [ddd, J(Rh,P_C) = 68 Hz, P_C] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 244.7 [dd, J(P,C) = 120, J(Rh,C) = 28 Hz, *C*O] ppm. **Data for 7b**. ^1H NMR ($CDCl_3$): δ = –7.46 [ddd, J(Rh,H) = 18.2, J(P,H)$_{trans}$ = 161.8, J(P,H)$_{cis}$ = 8.9 Hz, 1 H, RhH] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 65.8 [ddd, J(Rh,P_A) = 122, J(P_B,P_A) = 359, J(P_C,P_A) = 16 Hz, P_A], 58.6 [ddd, J(Rh,P_B) = 130, J(P_C,P_B) = 18 Hz, P_B], 28.5 [ddd, J(Rh,P_C) = 88 Hz, P_C] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 232.2 [d, J(Rh,C) = 32 Hz, *C*O] ppm. $C_{45}H_{38}ClOP_3Rh$ (827.09): calcd. C 65.35, H 4.75; found C 65.26, H 4.65.

[Rh(C_9H_6NCO){PPh_2(*o*-C_6H_4CO)}(NN)]BPh_4 [NN = 2,2′-bipyridine (8), 2-(aminomethyl)pyridine (9)]: To a dichloromethane solution of **2** (30 mg, 0.045 mmol) was added a stoichiometric amount of the corresponding ligand (0.045 mmol). After stirring at room temperature for 60 min, the solution was concentrated, and a methanol solution of $NaBPh_4$ (15.5 mg, 0.045 mmol) was added to afford a yellow precipitate, which was collected by filtration, washed with methanol and dried under vacuum. **Data for 8**: Yield 14 mg, 30%. IR (KBr): $\tilde{\nu}$ = 1663 (m), 1631 [s, ν(C=O)] cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 93 (acetone). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 65.2 [d, J(Rh,P) = 179 Hz] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 235.0 [d, J(Rh,C) = 31 Hz, *C*O], 229 [d, J(Rh,C) = 37 Hz, *C*O] ppm. $C_{63}H_{48}BN_3O_2PRh{\cdot}0.5CH_2Cl_2$ (1066.26): calcd. C 71.53, H 4.63, N 3.94; found C 71.70, H 4.62, N 4.08. **Data for 9**: Yield 27 mg, 62%. IR (KBr): $\tilde{\nu}$ = 3287 (m), 3237 [w, ν(NH)], 1660 (s), 1626 [s, ν(C=O)] cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 87 (acetone). ^1H NMR ($CDCl_3$): δ = 3.79 (br. s, 1 H, NH_2), 3.53 (m, 1 H, CH_2), 3.05 (m, 1 H, CH_2), 2.37 (br. s, 1 H, NH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 63.6 [d, J(Rh,P) = 166 Hz] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 237.0 [dd, J(Rh,C) = 31, J(P,C) = 10 Hz, *C*O], 233.2 [dd, J(Rh,C) = 35, J(P,C) = 3 Hz, *C*O] ppm. $C_{59}H_{48}BN_3O_2PRh$ (975.74): calcd. C 72.63, H 4.96, N 4.31; found C 71.93, H 4.94, N 4.38.

[RhCl(C_9H_6NCO)$_2$(py)] (11): To a MeOH suspension of **10** (22.5 mg, 0.025 mmol) was added pyridine (8.4 µL, 0.11 mmol). After stirring for 2 h, the yellow precipitate was collected by filtration and dried under vacuum; yield 19 mg, 67%. IR (KBr): $\tilde{\nu}$ = 1665 (s), 1630 [s ν(C=O)] cm^{-1}. $C_{25}ClH_{17}N_3O_2Rh$ (529.79): calcd. C 56.68, H 3.23, N 7.93; found C 56.69, H 3.25, N 7.72.

[Rh(C_9H_6NCO)$_2$(LL)]BPh_4 [LL = dppm (12), dppe (13), dppp (14), dppb (15), ampy (16), aqui (17), bdh (18), bipy (19)]: To a CH_2Cl_2/MeOH suspension of **10** (25 mg, 0.028 mmol) was added LL (0.056 mmol). After stirring for 30 min, dissolution occurred to give a light yellow solution. After stirring for a further 30 min, $NaBPh_4$ (19.2 mg, 0.056 mmol) was added to result in the immediate precipitation of yellow-orange solids, which were collected by

filtration, washed with methanol and dried under vacuum. **Data for 12**: Yield 42 mg, 65%. IR (KBr): $\tilde{\nu}$ = 1664 (s), 1640 [s, ν(C=O)] cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 93 (acetone). ^1H NMR ($CDCl_3$): δ = 4.20 [t, J(P,H) = 8.6, 2 H, CH_2] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –16.2 [d, J(Rh,P) = 63 Hz] ppm. $C_{69}H_{54}BN_2O_2P_2Rh{\cdot}0.5(CH_2Cl_2)$ (1161.34): calcd. C 71.88, H 4.77, N 2.41; found C 71.73, H 4.53, N 2.47. **Data for 13**: Yield 36 mg, 55%. IR (KBr): $\tilde{\nu}$ = 1659 (s), 1634 [s, ν(C=O)] cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 79 (acetone). ^1H NMR ($CDCl_3$): δ = 2.21 [d, J(P,H) = 10.0, 4 H, CH_2] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 27.9 [d, J(Rh,P) = 72 Hz] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 232.3 [dd, J(P,C) = 95, J(Rh,C) = 27 Hz, *C*O] ppm. $C_{70}H_{56}BN_2O_2P_2Rh{\cdot}CH_3OH$ (1164.94): calcd. C 73.20, H 5.19, N 2.40; found C 73.22, H 5.30, N 2.50. **Data for 14**: Yield 41 mg, 62%. IR (KBr): $\tilde{\nu}$ = 1658 (s), 1634 [s, ν(C=O)] cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 86 (acetone). ^1H NMR ($CDCl_3$): δ = 2.6–2.0 (m, 6 H, CH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –6.9 [d, J(Rh,P) = 70 Hz] ppm. $C_{71}H_{58}N_2O_2P_2BRh{\cdot}0.5CH_2Cl_2$ (1189.40): calcd. C 72.20, H 5.00, N 2.36; found C 71.99, H, 4.95, N 2.39. **Data for 15**: Yield 43 mg, 64%. IR (KBr): $\tilde{\nu}$ = 1656 (s), 1631 [s, ν(C=O)] cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 78 (acetone). ^1H NMR ($CDCl_3$): δ = 2.9–2.1 (m, 8 H, CH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –2.3 [d, J(Rh,P) = 66 Hz] ppm. $C_{72}H_{60}BN_2O_2P_2Rh{\cdot}0.5CH_2Cl_2$ (1203.42): calcd. C 72.36, H 5.11, N 2.33; found C 72.41, H 5.07, N 2.44. **Data for 16**: Yield 19 mg, 39%. IR (KBr): $\tilde{\nu}$ = 1669 (s), 1628 [s, ν(C=O)] cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 78 (acetone). ^1H NMR ($CDCl_3$): δ = 3.23–2.95 (m, 2 H, CH_2), 1.30 (m, 1 H, NH_2), 0.79 (m, 1 H, NH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 232.5 [d, J(Rh,C) = 33 Hz, *C*O], 226.9 [d, J(Rh,C) = 33 Hz, *C*O], 49.1 (s, *C*H_2) ppm. $C_{50}H_{40}BN_4O_2Rh{\cdot}CH_3OH$ (874.66): calcd. C 70.03, H 5.07, N 6.41; found C 70.18, H 4.25, N 6.49. **Data for 17**: Yield 22 mg, 43%. IR (KBr): $\tilde{\nu}$ = 1667 (s), 1628 [s, ν(C=O)] cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 78 (acetone). ^1H NMR ($CDCl_3$): δ = 3.39 (s, 2 H, NH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 235.5 [d, J(Rh,C) = 34 Hz, *C*O], 233.4 [d, J(Rh,C) = 33 Hz, *C*O] ppm. $C_{53}H_{40}BN_4O_2Rh{\cdot}CH_3OH$ (910.69): calcd. C 71.22, H 4.87, N 6.15; found C 71.33, H 4.59, N 6.17. **Data for 18**: Yield 28 mg, 57%. IR (KBr): $\tilde{\nu}$ = 1671 (s), 1636 [s, ν(C=O)] cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 88 (acetone). ^1H NMR ($CDCl_3$): δ = 5.22 (s, 4 H, NH_2), 1.63 (s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 231.2 [d, J(Rh,C) = 33 Hz, *C*O], 14.0 (s, *C*H_3) ppm. $C_{48}H_{42}BN_6O_2Rh{\cdot}0.5CH_2Cl_2$ (891.09): calcd. C 65.37, H 4.86, N 9.43; found C 65.20, H 5.05, N 9.50. **Data for 19**: Yield 29 mg, 56%. IR (KBr): $\tilde{\nu}$ = 1670 (s), 1637 [s, ν(C=O)] cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 91 (acetone). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 229.7 [d, J(Rh,C) = 33 Hz, *C*O] ppm. $C_{54}H_{40}BN_4O_2Rh{\cdot}CH_3OH$ (922.70): calcd. C 71.59, H 4.81, N 6.07; found C 71.74, H 4.87, N 6.12.

Catalytic Reactions: The transfer hydrogenation reactions were carried out under nitrogen in 2-propanol under reflux conditions with magnetic stirring. The equipment consisted of a 100 mL round-bottomed flask, fitted with a condenser and septum cap. The catalysts were prepared by adding KOH (0.2 mmol) in 2-propanol (10 mL) to solutions (30 mL) of the catalyst precursor (0.02 mmol). The resulting solutions were heated to 83 °C and the substrate (4 mmol) was injected. Analysis of the catalytic reactions was carried out with a Shimadzu GC-14A chromatograph, connected to a Shimadzu C-R6A calculation integrator.

X-ray Structure Determination of 2a: Prismatic yellow crystals of **2a** suitable for X-ray experiments were obtained by slow diffusion of diethyl ether into dichloromethane solutions. A summary of the fundamental crystal and refinement data are given in Table 2. A yellow crystal was coated with epoxy resin and mounted within a Bruker Smart CCD diffractometer with graphite-monochromated Mo-K_α (λ = 0.71073) radiation operating at 50 kV and 25 mA. Data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each frame exposure was of 20 s and covered 0.3° in ω. The cell parameters were determined and refined by least-squares fit of all reflections collected. The first 100 frames were recollected at the end of the data collection to monitor crystal decay, and no appreciable drop in the intensities was observed. An empirical absorption correction was performed. The structure was solved by direct methods and conventional Fourier techniques and refined by applying full-matrix least-squares on F^2 with anisotropic thermal parameters for the non-hydrogen atoms with exceptions: the solvent molecule was refined isotropically with restrained C–Cl distances. The hydrogen atoms were included at their calculated positions determined by molecular geometry and refined riding on the corresponding bonded atom. The largest first peaks in the final difference map are near to a solvent molecule. All the calculations were carried out with SHELX-97.[28]

Table 2. Crystal data and structure refinement for **2a**.

Empirical formula	$[C_{34}H_{25}ClN_2O_2PRh]CH_2Cl_2$
Formula mass	747.82
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	10.4539(6)
b [Å]	19.242(1)
c [Å]	16.536(1)
β [°]	104.438(1)
Volume [$Å^3$]	3221.1(3)
Z	4
Density (calcd.) [$g\,cm^{-3}$]	1.542
Absorption coefficient [mm^{-1}]	0.864
Scan technique	ω and ϕ
F(000)	1512
θ range [°]	1.65 to 25.00
Index ranges	(–11, –16, –19 to 12, 22, 13)
Reflections collected	16690
Independent reflections	5580 [R(int) = 0.0685]
Completeness to θ	100.0%
Data/restraints/parameters	5680/2/382
Goodness-of-fit on F^2	1.025
Final R[a] indices [$I > 2\sigma(I)$]	0.0720 (3442 observed)
wR_2[b] indices (all data)	0.2289
Largest diff. peak and hole [$e\,Å^3$]	2.369 and –1.234

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

CCDC-836821 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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