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Stereoselective formation and catalytic activity of hydrido(acylphosphane)(chlorido)(pyrazole)-rhodium(III) complexes. Experimental and DFT studies†

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The reaction of [{RhCl(COD)}$_2$] (COD = 1,5-cyclooctadiene) with L = pyrazole (Hpz), 3(5)-methylpyrazole (Hmpz) or 3,5-dimethylpyrazole (Hdmpz) and PPh$_2$(*o*-C$_6$H$_4$CHO) (Rh : L : P = 1 : 2 : 1) gives hydridoacyl complexes [RhHCl{PPh$_2$(*o*-C$_6$H$_4$CO)}(L)$_2$] (**1**). Stereoselective formation of **1-Hpz** and **1-Hmpz** with pyrazoles *trans* to hydrido and phosphorus and hydrogen bond formation with *O*-acyl and chlorido occur. **1-Hmpz** is a mixture of two linkage isomers in a 9 : 1 ratio, with two 5-methylpyrazole ligands or with one 3- and one 5-methylpyrazole ligand, respectively. Fluxional **1-Hdmpz** undergoes metallotropic tautomerization and is a mixture of equal amounts of **1a-Hdmpz** and **1b-Hdmpz**, with hydrido *trans* to pyrazole or chlorido, respectively. Complexes **1** readily exchange hydrido by chlorido to afford [RhCl$_2${PPh$_2$(*o*-C$_6$H$_4$CO)}(L)$_2$] (**2-Hpz**, **2-Hmpz** and **2-Hdmpz**) as single isomers with *cis* chloridos and two N–H···Cl hydrogen bonds. The reaction of **1** with PPh$_3$ or PPh$_2$OH affords static [RhHCl{PPh$_2$(*o*-C$_6$H$_4$CO)}(PPh$_3$)L] (**3**) or [RhHCl{PPh$_2$(*o*-C$_6$H$_4$CO)}(PPh$_2$OH)L] (**4**) respectively with *trans* P-atoms and pyrazoles forming N–H···Cl hydrogen bonds. **3-Hpz** and **3-Hmpz** contain single species with hydrido *cis* to chlorido, while **3-Hdmpz** is a mixture of equal amounts of **3a-Hdmpz** and **3b-Hdmpz**. Complexes **4**, with an additional O–H···O hydrogen bond, selectively contain only the *cis*-H,Cl species with all the three ligands. The reaction of [{RhCl(COD)}$_2$] with L and PPh$_2$(*o*-C$_6$H$_4$CHO) (Rh : L : P = 1 : 1 : 2) led to complexes with *trans* P-atoms, [RhHCl{PPh$_2$(*o*-C$_6$H$_4$CO)}{PPh$_2$(*o*-C$_6$H$_4$CHO)-κ*P*}L] (**5-Hpz**, **5a-Hdmpz** and **5b-Hdmpz**), at room temperature, and to [RhCl{PPh$_2$(*o*-C$_6$H$_4$CO)}{PPh$_2$(*o*-C$_6$H$_4$CHOH)}(Hmpz)] (**6-Hmpz**) or [RhCl-{PPh$_2$(*o*-C$_6$H$_4$CO)}$_2$L] (**7**) with hydrogen evolution in refluxing benzene. DFT calculations were used to predict the correct isomers, their ratios and the particular intramolecular hydrogen bonds in these complexes. Single crystal X-ray diffraction analysis was performed on **2-Hpz**, **3a-Hdmpz** and **7-Hpz**. Complexes **1** are efficient homogeneous catalysts (0.5 mol% loading) in the hydrolysis of amine– or ammonia–borane (AB) to generate up to 3 equivalents of hydrogen in the presence of air.

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Introduction

Acylhydrido transition metal species are well known to be involved in many stoichiometric and catalytic reactions such as hydroacylation[1] or aldehyde decarbonylation reactions,[2] among others. Recently we have reported that hydridoirida-β-diketones, which contain an acyl and a hydroxycarbene group stabilized by a strong O···H···O intramolecular hydrogen bond or {(acylphosphane)(diphenylphosphinous acid)}-rhodium(III) complexes, which contain a hydrogen bond between the acidic hydrogen atom of the coordinated phosphane and the oxygen atom of a coordinated acyl group, are efficient and robust homogeneous catalysts for the hydrolysis of ammonia– or amine–boranes under air to release hydrogen gas.[3] Pyrazoles, five-membered heterocycles containing two adjacent nitrogen atoms, possess a wide range of useful properties[4] and as ligands to transition metals they have attracted considerable interest.[5] Pyrazoles possess a planar aromatic

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† Electronic supplementary information (ESI) available: Cartesian coordinates of optimized DFT structures, images generated from those coordinate files, computationally obtained energy values associated with each structure, and crystallographic data file of complexes **2-Hpz**, **3a-Hdmpz** and **7-Hpz**. CCDC 1062495–1062497. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt01705j

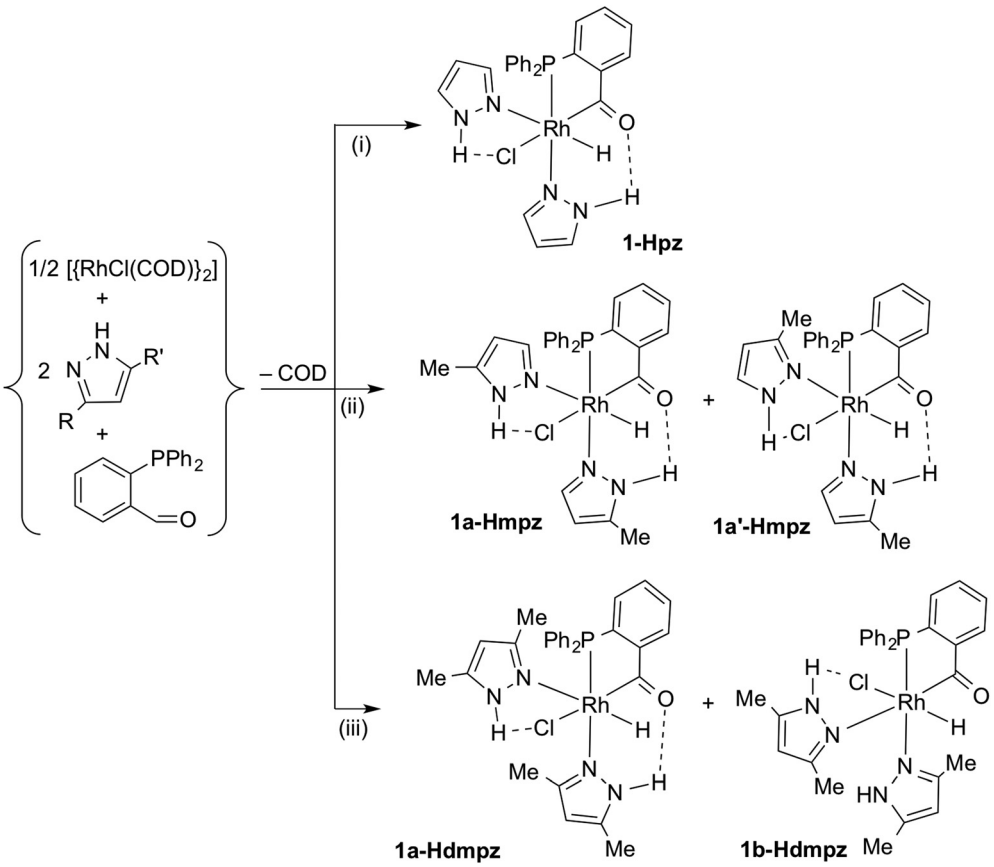
ring with a pyridine-type nitrogen suitable for coordination and an adjacent N–H group that can behave as a hydrogen-bond donor. In metal complexes of simple pyrazoles both inter- and intra-molecular hydrogen bonding can be found. Intermolecular forces have been successfully employed for the construction of supramolecular assemblies with various and interesting structures.[6] Intramolecular hydrogen bonds are important in establishing the conformation of the complexes.[7] Halide, hydroxide or peroxo species are known as hydrogen-bond acceptors towards metal-coordinated pyrazoles[8] and the presence of strong hydrogen bonds between pyrazole and pyrazolate moieties in late transition metal complexes has also been reported.[9] Therefore, we thought it interesting to prepare acylrhodium derivatives containing pyrazoles, which could form hydrogen bonds involving the oxygen atom of the acyl group and behave as catalysts for the hydrolysis of amine–boranes to release hydrogen. Hydrogen is a feasible alternative to fossil fuels but its safe storage and delivery still remains a challenge.[10] Ammonia–borane (AB), a chemical hydrogen storage material with high hydrogen contents (H_3N–BH_3, 19.6 wt%), is considered a potential hydrogen source. The homogeneous transition-metal catalysed dehydrogenation of ammonia– or amine–boranes under mild conditions, which usually affords up to one equivalent of hydrogen gas and requires an inert atmosphere, has been the subject of recent intensive research.[11] Hydrolysis reactions can afford up to three equivalents of hydrogen per equivalent of an amine–borane adduct. Transition metal heterogeneous systems,[12] which often require an inert atmosphere and include highly efficient rhodium nanoparticles,[13] allow fast H_2 release from these amine–borane adducts at room temperature. The efficient homogeneously catalyzed version of this reaction has been reported more recently using the afore-mentioned hydrido-irida-β-diketones or hydrido{(acylphosphane)(diphenylphosphinous acid)}rhodium(III) complexes,[3] and also iridium-PNP complexes,[14] coordinatively unsaturated iridium-carbene derivatives,[15] dicarbonylruthenacyclic compounds[16] or ruthenium-bipyridine-*p*-cymene complexes.[17]

We now report on the preparation of new hydrido(acylphosphane)rhodium(III) complexes containing pyrazole (Hpz), 3(5)-methylpyrazole (Hmpz) or 3,5-dimethylpyrazole (Hdmpz). DFT calculations were carried out aimed at identifying the thermodynamically most stable isomer of those complexes that could not be unambiguously characterized otherwise. The catalytic activity of the complexes to promote the hydrolysis of AB or amine–boranes in air to release hydrogen is also tested.

Results and discussion

The reaction of $[\{RhCl(COD)\}_2]$ (COD = 1,5-cyclooctadiene) with $PPh_2(o\text{-}C_6H_4CHO)$ (Rh/P = 1 : 1) in the presence of pyrazole (Rh/Hpz = 1 : 2) leads to the displacement of COD and the formation of the hydridoacyl complex $[RhHCl\{PPh_2(o\text{-}C_6H_4CO)\}(Hpz)_2]$ (**1-Hpz**), shown in Scheme 1i, in line with the well-known ability of the aldehyde-phosphane ligand to promote the chelate-assisted oxidative addition of the aldehyde to late transition metal complexes.[2e] The NMR spectra indicate the presence of only one species in solution. The $^{31}P\{^1H\}$ NMR spectrum contains only one doublet due to coupling with rhodium (J(Rh,P) = 166 Hz) at 79.0 ppm, the characteristic low field due to the five-member ring effect.[18] The ^1H NMR spectrum shows two sets of pyrazole signals at 8.47, 7.64 and 6.35 ppm or 7.00, 6.95 and 5.85 ppm, respectively, due to two non-equivalent ligands. These resonances are sharp and different for protons 3 and 5 of each pyrazole ring, indicating the absence of metallotropic tautomerization and both pyrazoles being firmly bonded to rhodium.[8,19] In the low field region, the N–H resonances, also sharp, appear at 14.02 and 11.75 ppm and suggest the presence of hydrogen bonding to oxygen and chlorido. Adscription of the former to N–H···O bonding between the acyl group and the pyrazole *trans* to phosphorus appears likely.[3d] A doublet of doublet in the high field region, due to a hydrido bonded to rhodium (J(Rh,H) = 21.0 Hz) and *cis* to phosphorus (J(P,H) = 15.4 Hz) is observed. The chemical shift, at −15.79 ppm, is consistent with a hydrido *trans* to an electronegative atom. Due to the equivalent *trans* influence exerted by chlorido and N-donor ligands,[20] it is difficult to determine the relative *cis*/*trans* disposition of the chlorido and the hydrido ligands. Also, the identification of the partners involved in the generation of intramolecular hydrogen bonds to the donor group of the pyrazole may be difficult due to the dependency of the hydrogen bond strength on its geometry, as well as on the nature of the substituent in the *trans* position to the acceptor ligand.[21] DFT calculations (see below) indicate the structure depicted in Scheme 1i, with hydrido *cis* to chlorido and *trans* to pyrazole, to be the most stable for **1-Hpz**.

The reaction with 3(5)-methylpyrazole affords a mixture of two isomers shown in Scheme 1ii, **1a-Hmpz** : **1a′-Hmpz** = 9 : 1. The spectroscopic features, similar to those observed for **1-Hpz**, indicate the absence of metallotropic tautomerization. In this case we believe that isomers **1a-Hmpz** and **1a′-Hmpz** are linkage isomers. 1*H*-Pyrazoles exist in solution as mixtures of two tautomeric forms whereas in the solid state, with very few exceptions, only one tautomer is observed.[4] When coordinated to transition metals, 3(5)-(R)pyrazoles (R = alkyl or aryl) usually appear in the 5-(R)pyrazole coordination mode, with the R group in the most distant position from the coordinating N-atom, in order to avoid steric congestion.[22] The tautomerism of 3(5)-methylpyrazole, involving the proton transfer between nitrogen sites has been thoroughly studied.[23] This ligand is unique and a few examples of complexes that contain both coordination modes, 5-methylpyrazole and 3-methylpyrazole, on the same metal atom have been reported.[6a,24] Due to steric constraints, in our case the most abundant isomer, **1a-Hmpz**, is expected to contain two less demanding 5-methylpyrazole ligands and the minor isomer, **1a′-Hmpz**, could contain at least one 3-methylpyrazole ligand. DFT calculations (*vide infra*) confirm this assumption and show that isomer **1a′-Hmpz**, containing both coordination modes 5- and 3-methylpyrazole, must be the minor linkage isomer.



Scheme 1 In C_6H_6, 298 K. (i) R = R′ = H, Hpz; (ii) R = Me, R′ = H, Hmpz; (iii) R = R′ = Me, Hdmpz.

When the reaction is performed using 3,5-dimethylpyrazole, a different behaviour is observed. The ^{1}H and ^{31}P{^{1}H} NMR spectra at 298 K indicate the presence of almost equal amounts of the two species **1a-Hdmpz** and **1b-Hdmpz** in solution. The ^{31}P{^{1}H} NMR spectrum contains two doublets in the 77–78 ppm range and the ^{1}H NMR spectrum shows two doublets of doublets in a very narrow range, between −15.5 and −16.5 ppm, due to the corresponding hydridos. We believe that both isomers differ in the group *trans* to hydrido as shown in Scheme 1iii, pyrazole in **1a-Hdmpz** or chlorido in **1b-Hdmpz**. DFT calculations (see below) confirm the similar stability of these complexes, **1a-Hdmpz** and **1b-Hdmpz**. Furthermore, in the ^{1}H NMR spectrum, the resonances due to the pyrazole groups are extremely broad, suggesting that both isomers undergo metallotropic tautomerization and proton transfer in addition to metal exchange between nitrogen sites.[6b,22a,b,25] The metallotropic tautomerization is much less frequent than that observed for the free ligands. On lowering the temperature, the signals due to the pyrazole become sharper, so that by 213 K the expected resonances due to four non-equivalent groups, two per isomer, with eight non-equivalent methyl groups, can be observed. These results show that at low temperatures the metallotropic tautomerization, which can be attributed to steric congestion, becomes inhibited. The resonances due to the phosphanes and the hydridos remain unaltered in the 298–213 K range.

Complexes **1** are stable at room temperature in the solid state but show low stability in solution, therefore single crystals for a crystallographic study could not be obtained. As mentioned earlier, theoretical calculations were performed to determine the particular disposition of the ligands around the central metal and to describe the intramolecular hydrogen bonds established in the obtained compounds. On the basis of its reported accuracy,[26] the M062X level DFT calculations were carried out in order to identify the most stable isomers and rotamers, involving different hydrogen bonding options, of complexes **1**. Comparison of PCM corrected relative ΔG values for all possible isomers and rotamers of compounds **1** at the M062X level was shown to be an appropriate tool to identify the thermodynamically most stable isomer/rotamer in each case. The absolute Gibbs free energies of the most stable structures (Tables 1 and SI-1, ESI†) were used in each case to estimate the relative stability (ΔG) of the rotamers/isomers.

Up to 12 alternative isomers/rotamers with chlorido *cis* to phosphorus were considered in the case of **1-Hpz**-type structures (Table SI-1†). The isomer with chlorido *trans* to phosphorus and both Hpz ligands *cis* to each other was found to be 12.51 kcal mol^{-1} less stable than compound **1-Hpz** (data not

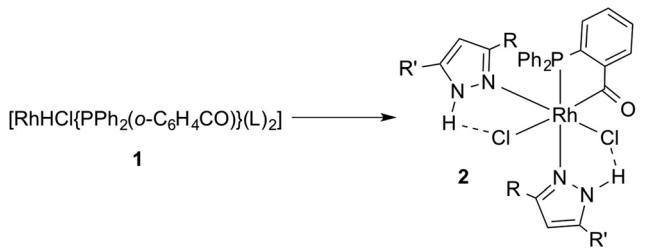
Table 1 Ranked PCM corrected relative free energy values (ΔG, kcal mol^{-1}) calculated at the M062X/6-311++G(2d,2p)//B3LYP/6-31G(d,p)& LANL2DZ level of theory, for the most stable isomers/rotamers of compounds **1-Hpz**, **1-Hmpz** and **1-Hdmpz**, respectively

Compound type		ΔG_{solv}	*cis*/*trans* H,Cl-disposition[a]	R/R′		H-bond	
				trans[b]	*cis*[c]	*trans*[d]	*cis*[e]
1-Hpz	**1-Hpz**	0.00	*cis*-H,Cl	H/H	H/H	*O*-Acyl	Chlorido
1-Hmpz	**1a-Hmpz**	0.00	*cis*-H,Cl	H/Me	H/Me	*O*-Acyl	Chlorido
	1a′-Hmpz	1.35	*cis*-H,Cl	H/Me	Me/H	*O*-Acyl	Chlorido
1-Hdmpz	**1b-Hdmpz**	0.00	*trans*-H,Cl	Me/Me	Me/Me	*O*-Acyl	Chlorido
	1b′-Hdmpz	0.02	*trans*-H,Cl	Me/Me	Me/Me	Chlorido	Chlorido
	1a-Hdmpz	0.35	*cis*-H,Cl	Me/Me	Me/Me	*O*-Acyl	Chlorido

[a] *cis* or *trans* disposition of chlorido with respect to hydrido. [b] Nature of R and R′ in the pyrazole *trans* to phosphorus. [c] Nature of R and R′ in the pyrazole *cis* to phosphorus. [d] Acceptor group of the hydrogen bond established by the pyrazole *trans* to the phosphorus atom. [e] Acceptor group of the hydrogen bond established by the pyrazole *cis* to the phosphorus atom.

shown). In view of this significant thermodynamic destabilization, the theoretical study of additional *trans* (chlorido/phosphorus) isomers was found unnecessary. As observed in Table 1, the *cis*-H,Cl isomer **1-Hpz** was identified as the most stable and unique structure, since the energetically closest structure, a *trans*-H,Cl isomer, turned out to be 1.86 kcal mol^{-1} less stable (Table SI-1†), a significant energy difference, which rules out the possibility of the experimental observation of both species in the NMR spectra. This is in agreement with the experimental data. Compound **1-Hpz** corresponds therefore to the *cis*-H,Cl isomer shown in Fig. SI-1a,† where the pyrazoles *trans* and *cis* to phosphorus would establish hydrogen bonds with the acceptors *O*-acyl and chlorido, respectively. Any rotamer/isomer where the hydrido acts as a hydrogen bond acceptor was shown to be consistently unstable with respect to **1-Hpz** (see Fig. SI-2†). With respect to **1-Hmpz**-type structures, the inclusion of all plausible tautomeric species led to the analyses of 48 structures, which, again, cover all plausible combinations of intramolecular hydrogen bonds (Table SI-1†). As shown in Table 1, complexes **1a-Hmpz** and **1a′-Hmpz** were identified as the major and minor species (9 : 1), respectively, as concluded from the significant energy difference among the two (ΔG = 1.35 kcal mol^{-1}). As observed in Fig. SI-1 (b and c),† compounds **1a-Hmpz** and **1a′-Hmpz** are tautomeric species, where the pyrazole *cis* to phosphorus is methylated either on the 5- or 3-position, respectively. Both of them are *cis*-H,Cl isomers.

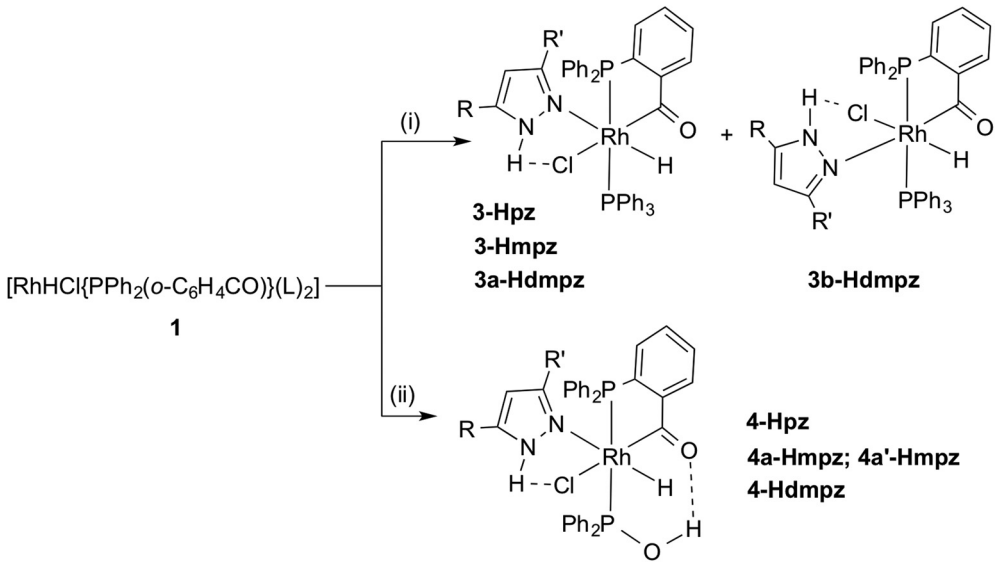
Experimental NMR data for **1-Hdmpz**-type compounds revealed the existence of almost equimolar amounts of two species. In agreement with this, DFT results pointed out that two or even three species may exist simultaneously in solution. A slightly more abundant species (60%) was identified to consist of two rotamers of the *trans*-H,Cl isomer, **1b-Hdmpz** and **1b′-Hdmpz** (Fig. SI-1d and e†), where the pyrazole *trans* to phosphorus would establish alternating hydrogen bonds with the *O*-acyl (**1b-Hdmpz**) and the chlorido (**1b′-Hdmpz**), respectively (ΔG = 0.02 kcal mol^{-1}). The *cis*-H,Cl isomer **1a-Hdmpz** (Fig. SI-1f†) would be a slightly less abundant species (40%), with a moderate energy difference with the former (ΔG = 0.35 kcal mol^{-1}). We thus observe that the difference in energy between *trans*-H,Cl and *cis*-H,Cl isomers is much smaller for the Hdmpz ligand than for the Hpz or Hmpz ligands, and allows the formation of both isomers in the Hdmpz case. In an attempt to identify the driving force that provokes the lower stability difference between isomers, steric clashes between the methyl groups present as substituents on the Hdmpz ligand (*cis* to phosphorus and also *cis* to acyl) with the neighbouring *O*-acyl were encountered. This steric effect would destabilize the *cis*-H,Cl geometry reducing the energy gap with the *trans*-H,Cl geometry, containing a Hdmpz ligand *trans* to acyl.



Scheme 2 In $CHCl_3$, 298 K. **2-Hpz**, R = R′ = H; **2-Hmpz**, R = H, R′ = Me; **2-Hdmpz**, R = R′ = Me.

In a chloroform solution complexes **1** readily exchange the hydrido with chlorido to afford complexes [$RhCl_2${PPh_2-(o-C_6H_4CO)}$(L)_2$] (L = Hpz, **2-Hpz**; Hmpz, **2-Hmpz**; Hdmpz, **2-Hdmpz**). Such a reaction has several precedents.[27] As shown in Scheme 2, in all the three cases single species are obtained, which are static in solution on the NMR time scale at room temperature. An X-ray diffraction study on complex **2-Hpz** (see below) indicates *cis* chloridos and the existence of N–H···Cl hydrogen bonds.

It is remarkable that upon exchange of hydrido by chlorido, the ^{31}P NMR signal moves significantly towards a higher field and appears in the 57–59 ppm range. A reduction in the coupling constant, J(Rh,P) = 136 Hz, is also observed. Their $^{13}C\{^1H\}$ NMR spectra show the resonance due to the acyl group in the low field, 222–228 ppm range, as a doublet of doublet due to



Scheme 3 In CH_2Cl_2, 298 K. (i) PPh_3: **3-Hpz**, R = R′ = H; **3-Hmpz**, R = Me, R′ = H; **3a-Hdmpz** and **3b-Hdmpz**, R = R′ = Me. (ii) $PPh_2(O)H$: **4-Hpz**, R = R′ = H; **4a-Hmpz**, R = Me, R′ = H; **4a′-Hmpz**, R = H, R′ = Me; **4-Hdmpz**, R = R′ = Me.

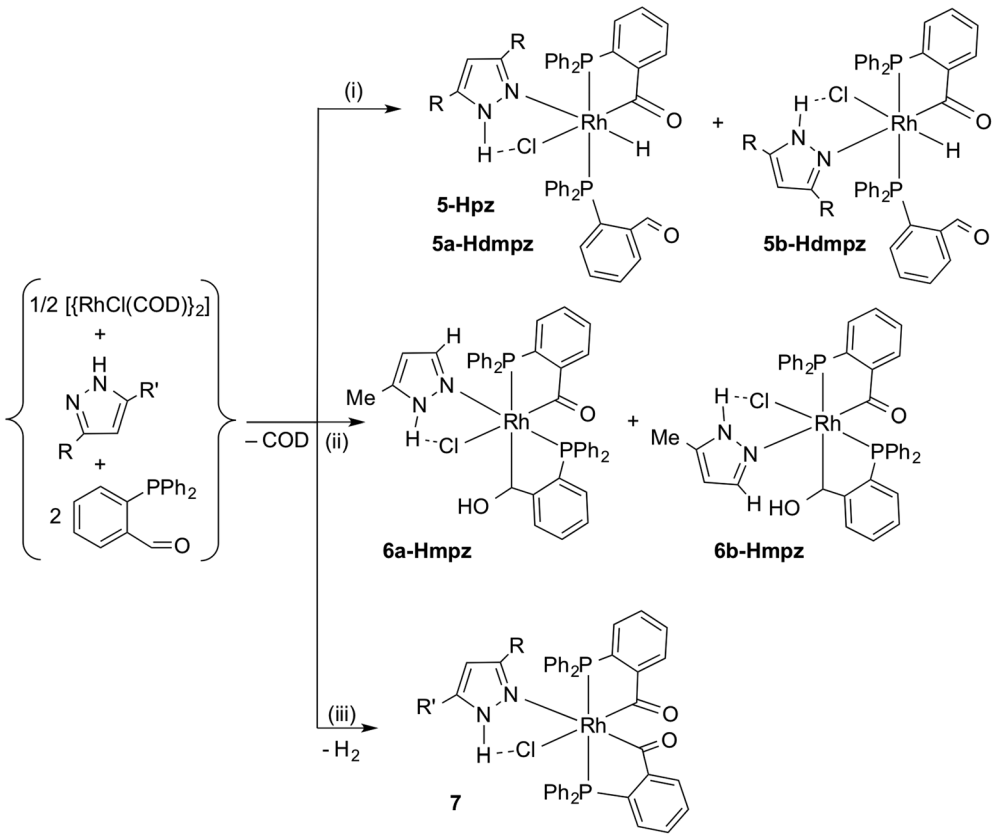
coupling with rhodium (J(Rh,C) = 28 Hz) and with a *cis* phosphorus atom (J(P,C) = 3 Hz).

Complexes **1** react with triphenylphosphane that displaces the pyrazole ligand *trans* to phosphorus to give complexes [RhHCl{PPh_2(*o*-C_6H_4CO)}(PPh_3)L] (L = Hpz, **3-Hpz**; Hmpz, **3-Hmpz**; Hdmpz, **3a-Hdmpz** and **3b-Hdmpz**) as shown in Scheme 3i. The reaction is stereoselective for Hpz and Hmpz affording only one isomer, which, in accord with the DFT studies performed for complexes **1**, we assume to be the *cis*-H, Cl species, while Hdmpz affords an almost equimolar mixture of two isomers that, as shown by the NMR spectra, can only differ in the group *trans* to the hydrido, pyrazole in **3a-Hdmpz** or chlorido in **3b-Hdmpz**.

The $^{31}P\{^1H\}$ NMR spectra show two doublets of doublets in the 65–62 and the 44–38 ppm range, due to the chelating acylphosphane and PPh_3 respectively. The J(P,P) coupling constants, in the 376–379 Hz range, indicate two mutually *trans* phosphorus atoms. In the $^{13}C\{^1H\}$ NMR spectra, the resonance due to the acyl group appears as a doublet (J(Rh,C) in the range 28–35 Hz) in the expected low field (232–235 ppm range),[28] and the resonances due to the 3 and 5 carbon atoms of the pyrazole rings are different, indicating the absence of tautomerization in all cases. In the ^1H NMR spectra, the hydrido appears as a doublet of doublet of doublet due to coupling to rhodium and to two *cis* phosphorus atoms, in the −14.0 to −14.5 ppm range, in a slightly lower field than in complexes **1**. Sharp singlets in the 11.0–11.8 ppm range are also observed, due to the pyrazole being involved in N–H···Cl hydrogen bonding, and the resonances for protons or methyl groups on the 3 and 5 carbon atoms of the pyrazole rings are different. An X-ray diffraction study of **3a-Hdmpz** confirms the structure depicted in Scheme 3i.

The reaction of complexes **1** with diphenylphosphane oxide affords complexes [RhHCl{PPh_2(*o*-C_6H_4CO)} {(PPh_2O)H} L] (L = Hpz, **4-Hpz**; Hmpz, **4a-Hmpz** and **4a′-Hmpz**; Hdmpz, **4-Hdmpz**) shown in Scheme 3ii. As in the reaction with PPh_3, **1-Hpz** affords a single isomer **4-Hpz**. **1-Hmpz** gives two linkage isomers, **4a-Hmpz** : **4a′-Hmpz** = 9 : 1, as in the starting material. At variance with the reaction with PPh_3, **1-Hdmpz**, which consists of an almost equimolar mixture of two isomers, affords now a single isomer **4-Hdmpz**. The spectroscopic features of complexes **4** are similar to those reported for complexes **3** (see Experimental). In the low field region of the ^1H NMR spectra, a sharp singlet is observed, in the 10.7–11.2 ppm range due to N–H···Cl. Another sharp singlet is observed in the 12.0–12.7 ppm range that can be attributed to the presence of a hydrogen bond between the oxygen atom of the diphenylphosphinous acid and the oxygen atom of the coordinated acyl group.[3d,29] This O–H···O hydrogen bond appears to contribute to the stereoselectivity of this reaction to afford a single isomer also in the Hdmpz case. DFT calculations (see below) show this isomer to be the *cis*-H,Cl species.

In accordance with these observations, the preparation of complexes [RhHCl{PPh_2(*o*-C_6H_4CO)}{PPh_2(*o*-C_6H_4CHO)-κ*P*}L] (L = Hpz, **5-Hpz**; Hdmpz, **5a-Hdmpz** and **5b-Hdmpz**), by reaction of [{RhCl(COD)}$_2$] with PPh_2(*o*-C_6H_4CHO) in the presence of pyrazoles (Rh/Hpz/P = 1 : 1 : 2), leads to a mixture of two isomers **5a-Hdmpz** : **5b-Hdmpz** = 7 : 3 when using Hdmpz while Hpz leads to a single isomer, **5-Hpz** (Scheme 4i). Complexes **5** contain a P-monodentate phosphane–aldehyde ligand with a dangling aldehyde group less suitable for hydrogen bond formation. The spectroscopic features of complexes **5** are as expected (see Experimental). When using Hmpz, the NMR spectra show the formation of a mixture of the corresponding



Scheme 4 (i) In C_6H_6, 298 K. **5-Hpz**, R = R′ = H; **5a-Hdmpz** and **5b-Hdmpz**, R = R′ = CH_3. (ii) In C_6H_6, 353 K, 5 min. (iii) In C_6H_6, 353 K, 90 min. **7-Hpz**, R = R′ = H; **7-Hmpz**, R = H, R′ = CH_3; **7-Hdmpz**, R = R′ = CH_3.

complex with a dangling aldehyde, **5-Hmpz**, which could not be obtained pure, and a hydroxyalkyl-phosphane derivative **6-Hmpz**, which is the product of the insertion of an aldehyde into the Rh–H bond.[27e,30]

Complex [RhCl{PPh_2(*o*-C_6H_4CO)}{PPh_2(*o*-C_6H_4CHOH)}-(Hmpz)], **6-Hmpz**, could be obtained in refluxing benzene (5 min) as shown in Scheme 4ii. It is a mixture of two isomers **6a-Hmpz** : **6b-Hmpz** in a 6 : 4 ratio, analogous to our previously reported pyridine containing species [RhCl{PPh_2(*o*-C_6H_4CO)}-{PPh_2(*o*-C_6H_4CHOH)}(py)].[27e] The $^{13}C\{^1H\}$ NMR spectrum shows a doublet of doublets in the 90–95 ppm range (J(Rh,C) = 22; J(P,C) = 100 Hz) showing the formation of hydroxyalkyl groups bonded to rhodium and *trans* to the phosphorus atom of the acyl-phosphane chelate. Accordingly, the $^{31}P\{^1H\}$ NMR spectrum shows two doublets of doublets for each isomer with phosphanes mutually *cis* (J(P,P) in the 16–19 Hz range). Isomers **6a-Hmpz** and **6b-Hmpz** differ in the group, chlorido or pyrazole, *trans* to acyl. Sharp singlets at 12.09 and 11.49 ppm in the ^1H NMR spectrum, can be attributed to N–H···Cl hydrogen bonds. Longer reaction times led to the formation of the diacyl derivative [RhCl{PPh_2-(*o*-C_6H_4CO)}$_2$(Hmpz)] (**7-Hmpz**) as a single isomer, with hydrogen evolution (see Scheme 4iii). Hpz and Hdmpz also afford complexes **7-Hpz** and **7-Hdmpz** respectively. The $^{31}P\{^1H\}$ NMR spectra of complexes 7 show ABX spin patterns with J(P,P) = 340 Hz, indicating the *trans* disposition of both phosphorus atoms while the $^{13}C\{^1H\}$ NMR spectra show in the low field region two doublets due to two inequivalent acyl groups *trans* to chlorido and pyrazole respectively. An X-ray diffraction study of **7-Hpz** confirms the structure depicted in Scheme 4iii.

The same theoretical study as before was carried out to identify the particular isomers/rotamers obtained for **3-Hdmpz**-, **4-Hdmpz**- and **5-Hdmpz**-type complexes. Phosphorus atoms were considered to be in the *trans* position to each other in all cases since NMR data for the mentioned complexes were unambiguous in this respect. Structures with intramolecular hydrogen bonds established between Hdmpz and any acceptor atom other than chlorido were not considered in these cases (Table SI-2†), since our DFT studies on complexes **1** have shown that pyrazole ligands *cis* to phosphorus form hydrogen bonds exclusively with chlorido. DFT results (Table 2) for **3-Hdmpz**-type complexes revealed that two species with a moderate energy difference (0.60 kcal mol^{-1}) may exist in a 3 : 7 ratio, namely, the *cis*-H,Cl **3a-Hdmpz** and the *trans*-H,Cl **3b-Hdmpz** isomers (Fig. SI-3a and b,† respectively), the *trans*-H,Cl isomer being the most abundant species. The latter result is similar to that previously described for **1-Hdmpz** and agrees with the experimental NMR data, which show the presence of two different species in solution. In the case of **4-Hdmpz**-type complexes, and in agreement with

Table 2 Ranked PCM corrected relative free energy values (ΔG, kcal mol^{-1}) calculated at the M062X/6-311++G(2d,2p)//B3LYP/6-31G(d,p)& LANL2DZ level of theory, for the most stable isomers/rotamers of compounds **3-Hdmpz**, **4-Hdmpz** and **5-Hdmpz**, respectively

Compound type		ΔG_{solv}	*cis*/*trans*[a]	H-bond	
				OH/CHO[b]	Pyrazole[d]
3-Hdmpz	**3b-Hdmpz**	0.00	*trans*-H,Cl		Chlorido
	3a-Hdmpz	0.60	*cis*-H,Cl		Chlorido
4-Hdmpz	**4-Hdmpz**	0.00	*cis*-H,Cl	*O*-Acyl	Chlorido
5-Hdmpz	**5a-Hdmpz**	0.00	*cis*-H,Cl	Hydrido[c]	Chlorido
	5b-Hdmpz	0.82	*trans*-H,Cl	*O*-Acyl[c]	Chlorido

[a] cis or *trans* disposition of chlorido with respect to hydrido. [b] Acceptor group of the hydrogen bond established by OH in **4-Hdmpz** or H in CHO of **5-Hdmpz**. [c] Considering the moderate polarity of the C–H bond in aldehydes, the quantitative significance of the indicated hydrogen bonds may be modest. Still they could be identified based on the directionality of the groups involved. The oxygen atom in CHO of **5-Hdmpz** was found to not be able to establish hydrogen bonds. [d] Acceptor group of the hydrogen bond established by the pyrazole.

the NMR data, the *cis*-H,Cl isomer **4-Hdmpz** was predicted to be the only species in solution (Fig. SI-3c†). The energy difference (2.99 kcal mol^{-1}) with the energetically closest structure ruled out any other possibility (Table SI-2†). As depicted in Fig. SI-3c,† the acidic hydrogen atom belonging to the diphenylphosphinous acid would establish a hydrogen bond with the *O*-acyl moiety. In this case, a combination of a lesser steric hindrance of PPh_2OH *versus* PPh_3 along with fixation of the *O*-acyl atom by O–H···O bond formation, relieves the steric clashes between pyrazole methyl substituents and the neighbouring *O*-acyl, thus stabilizing the *cis*-H,Cl conformation. Theoretical calculations on **5-Hdmpz**-type complexes revealed that the **5a-Hdmpz** *cis*-H,Cl isomer is 0.82 kcal mol^{-1} more stable that the *trans*-H,Cl isomer **5b-Hdmpz** (Table 2) and that both isomers may exist in an 8 : 2 ratio. The latter results are in agreement with the corresponding NMR data, which contain signals due to two different species in solution. As observed in Fig. SI-3d and SI-3e† a quantitatively significant N–H···Cl intramolecular bond is established, while a second hydrogen bond, which may be quantitatively much less meaningful, is also observed between the hydrogen atom of the aldehyde moiety and either the hydrido (**5a-Hdmpz**) or the *O*-acyl group (**5b-Hdmpz**). A visual inspection of **5a-Hdmpz** and **5b-Hdmpz** suggests a suboptimal spatial disposition of the acyl-phosphane ligand in the *trans*-H,Cl isomer, derived from its attempt to establish a H-bond with the H atom of the aldehyde moiety of the $PPh_2(o\text{-}C_6H_4CHO)$ ligand, which could rationalize the observed isomer ratios.

The X-ray structures of **2-Hpz** (dichloromethane adduct), **3a-Hdmpz** (chloroform adduct) and **7-Hpz** have been determined. Selected bond distances and angles are listed in Table 3. Fig. 1–3 show molecular drawings for these complexes together with the atomic labelling scheme used. All the three complexes show a slightly distorted octahedral arrangement, with two positions occupied by the phosphorus and carbon atoms of an acyl-phosphane ligand and a chlorido ligand *trans* to the acyl carbon atom. **2-Hpz** also contains two mutually *cis* pyrazole ligands that are *trans* to a second chlorido and to phosphorus. Compounds **3a-Hdmpz** or **7-Hpz** contain a single pyrazole ligand and hydrido and triphenylphosphane or a second acyl-phosphane ligand, respectively. In the latter compounds the pyrazole ligand lies *trans* to hydrido or to an acyl carbon atom, respectively, thus allowing the phosphorus atoms to adopt a *trans* arrangement. The Rh1–N1 distances: 2.046(2), 2.205(2) and 2.221(6) in **2-Hpz**, **3a-Hdmpz** and **7-Hpz** respectively and the Rh1–N3 distance of 2.136(2) Å in **2-Hpz** reflect the *trans* influence order of the ligands: chlorido <

Table 3 Selected bond lengths (Å) and angles (°) for **2-Hpz**, **3a-Hdmpz** and **7-Hpz**, including the intramolecular hydrogen bonding

2-Hpz		**3a-Hdmpz**		**7-Hpz**	
Rh1–N1	2.046(2)	Rh1–N1	2.205(2)	Rh1–N1	2.221(6)
Rh1–N3	2.136(2)	Rh1–P2	2.3443(9)	Rh1–P2	2.351(3)
Rh1–P1	2.2415(6)	Rh1–P1	2.2628(9)	Rh1–P1	2.318(3)
Rh1–Cl1	2.5491(5)	Rh1–Cl1	2.5073(6)	Rh1–Cl1	2.523(2)
Rh1–Cl2	2.3614(5)	Rh1–H1	1.401(4)	Rh1–C20	2.004(8)
Rh1–C1	1.992(2)	Rh1–C1	1.990(2)	Rh1–C1	2.01(1)
C1–O1	1.208(3)	C1–O1	1.216(4)	C1–O1	1.21(1)
N3–N4	1.349(3)			C20–O2	1.20(1)
N1–N2	1.347(2)	N1–N2	1.361(2)	N1–N2	1.35(1)
Cl1–Rh1–C1	179.02(7)	Cl1–Rh1–C1	176.94(9)	Cl1–Rh1–C1	173.1(3)
Cl2–Rh1–N1	175.71(5)	P1–Rh1–P2	171.98(3)	P1–Rh1–P2	168.35(9)
Cl1–Rh1–N1	89.14(5)	Cl1–Rh1–N1	87.71(7)	Cl1–Rh1–N1	85.8(2)
P1–Rh1–N3	177.95(5)	N1–Rh1–H1	178(2)	C20–Rh1–N1	173.1(3)
N2···Cl1	3.031(2)	N2···Cl1	3.067(3)	N2···Cl1	3.017(8)
H2N···Cl1	2.3073(5)	H2N···Cl1	2.4582(8)	H2N···Cl1	2.399(2)
N2–H2N···Cl1	140.3(1)	N2–H2N···Cl1	128.4(5)	N2–H2N···Cl1	129.3(5)
N4···Cl2	3.034(2)				
H4N···Cl2	2.3376(6)				
N4–H4N···Cl2	130.3(1)				

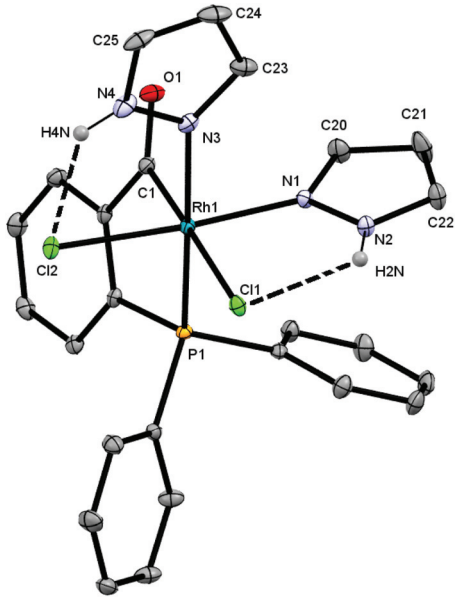


Fig. 1 ORTEP view of **2-Hpz** showing the atomic numbering and the intramolecular hydrogen bonds (30% probability ellipsoids). The hydrogen atoms except for two have been omitted for clarity.

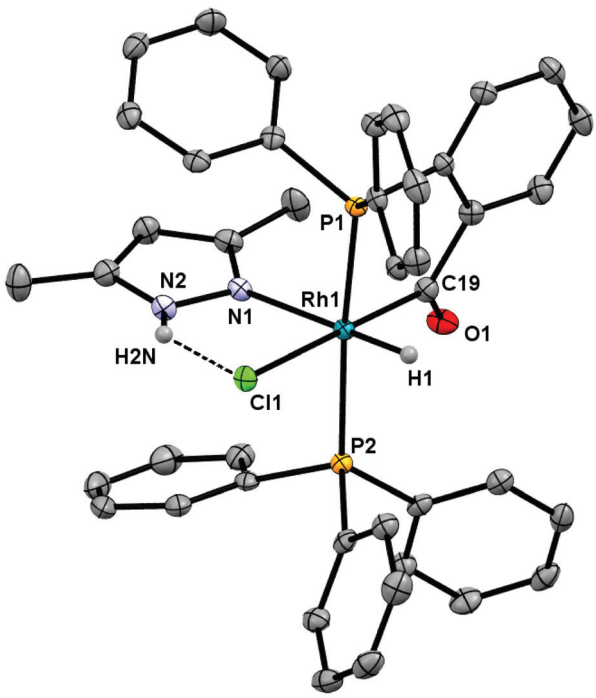


Fig. 2 ORTEP view of **3a-Hdmpz** showing the atomic numbering and the intramolecular hydrogen bond (30% probability ellipsoids). The hydrogen atoms except for two have been omitted for clarity.

phosphane < hydrido ≈ acyl.[31] In all the three structures the pyrazole moieties and the chlorido ligands are mutually *cis* and the formation of N–H···Cl hydrogen bonds is observed.

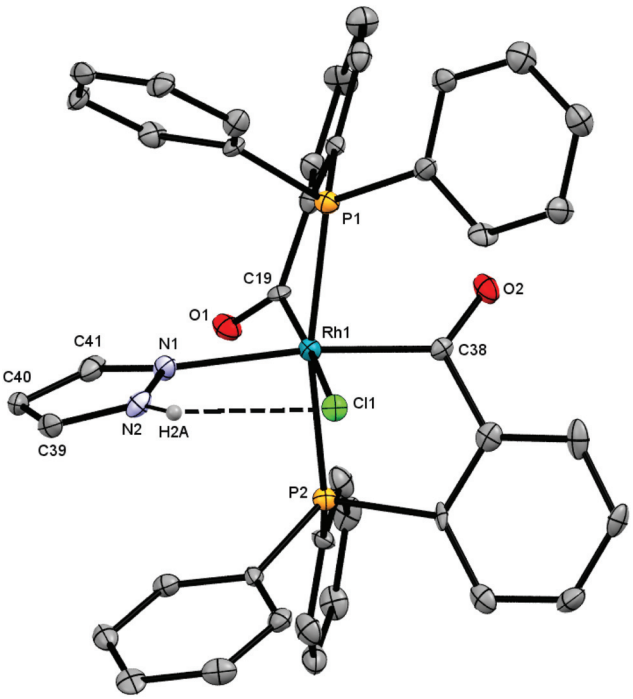


Fig. 3 ORTEP view of **7-Hpz** showing the atomic numbering and the intramolecular hydrogen bond (30% probability ellipsoids). The hydrogen atoms except for one have been omitted for clarity.

The pyrazole protons involved in these hydrogen bonds could be clearly located as Fourier peaks in a difference map. The N···Cl distances, between 3.017 Å and 3.067 Å, for all the three complexes are as expected for moderately strong hydrogen bonds, however the N–H···Cl angles, between 128(1) and 140(1)°, are in the lower range of the corresponding values.[7,32] Nevertheless, the importance of the hydrogen bonding can also be assessed by the dihedral angle between two planes, that of the pyrazole ring (including the N–H bond) and the plane defined by the coordinated N atom of pyrazole, chlorido, and their *trans* atoms to the metal and the metal, which should be close to 0°.[8] In **2-Hpz** these angles are very small, 4.8 and 6.6° for the planes involving the N4 and N2 atoms, respectively, indicating that the N–H vector is directed in order to maximize the intramolecular hydrogen bonding. For **3a-Hdmpz** and **7-Hpz** the values of these dihedral angles are 9.8 and 13.7°, respectively. In **2-Hpz** the planes of the heterocycles are almost perpendicular (θ = 86.8°), and this feature may be related to the presence of the hydrogen bonds. Also in **2-Hpz** the chlorido *trans* to acyl forms another hydrogen bond, N2–H2N···Cl1″, weaker, with the pyrazole *trans* to chlorido in a neighbouring molecule (N2–Cl1″ = 3.241(2) Å). This intermolecular interaction leads to the formation of dimers.

Complexes **1** and **4**, containing N–H···O or O–H···O hydrogen bonds respectively involving the acyl groups, were tried as catalysts for the hydrolysis of AB, TBAB (*tert*-butylamine-borane), and DMAB (dimethylamine-borane) in THF/H_2O = 1/1 mixtures, at 298 K, in the presence of air. According to eqn (1),

Table 4 % Conversion and time required, for the hydrolysis of ammonia– and amine–boranes with complexes **1** or **4** (0.5 mol%) in THF/H_2O = 1 : 1 ratio, at 298 K

Substrate	Catalyst	% Conv.	Time/s	Catalyst	% Conv.	Time/s
AB	**1-Hpz**	75	1500	**4-Hpz**	92	3000
	1-Hmpz	90	1500	**4-Hmpz**	90	3300
	1-Hdmpz	88	1500	**4-Hdmpz**	85	3600
TBAB	**1-Hpz**	81	1500	**4-Hpz**	78	3600
	1-Hmpz	75	1800	**4-Hmpz**	82	3600
	1-Hdmpz	79	1500	**4-Hdmpz**	82	3000
DMAB	**1-Hpz**	75	2400	**4-Hpz**	74	8400
	1-Hmpz	81	2400	**4-Hmpz**	80	5400
	1-Hdmpz	85	1800	**4-Hdmpz**	88	4200

up to three equivalents of hydrogen per equivalent of an adduct may be released.

$$RR'HN{-}BH_3 + 4H_2O \rightarrow RR'NH_2^+ + B(OH)_3 + OH^- + 3H_2 \quad (1)$$

With an initial AB, TBAB or DMAB concentration of 0.46 M and a 0.5 mol% catalyst loading of complexes **1**, the hydrolysis and the release of 75–90% of the maximum hydrogen content that could be produced, was observed within 25 min (Table 4). The nature of the product gas was verified as H_2 by NMR of the catalytic hydrolysis of AB in a THF-d_8/D_2O mixture, which shows the gradual disappearance of the quartet centred at δ = 1.37 ppm ($^1J_{B-H}$ = 92 Hz) due to AB and the formation of HD at δ = 4.52 (t) ppm ($^1J_{D-H}$ = 43 Hz). Blank tests under the same experimental conditions, but in the absence of a catalyst, show that the hydrolysis of AB, TBAB or DMAB affords a maximum amount of only 10% of the hydrogen content after 4 min Fig. SI-4†).

The catalytic activity for complexes **1-Hpz**, **1-Hmpz** and **1-Hdmpz** was similar. As shown in Fig. 4, the amount of hydrogen evolved from all the three substrates was analogous. When using complexes **4** a similar hydrogen release requires at least 50 min reaction times (Table 4). After completion of the catalytic reactions, the ^{11}B NMR spectra of the remaining solutions contain only singlets in the 16–20 ppm range, which indicates the transformation of the borane adducts into borate species.[13a,b] In the presence of Hg similar results were obtained, confirming the homogeneous nature of the catalytic reaction.[13c] Fig. 4 shows the kinetic profiles when using **1-Hmpz** as a catalyst. The kinetic profiles obtained in the hydrolysis of AB and TBAB can be considered to follow a first order reaction rate model with respect to the [substrate]. When the experimental points are fitted to a first order law by non-linear least-squares regression, the values of the rate constants k_{obs} = (1.89 ± 0.06) × 10^{-3} and (1.98 ± 0.10) × 10^{-3} s^{-1} can be obtained respectively for AB and TBAB. The kinetic profile of the hydrolysis of DMAB does not show a defined kinetic model. The activity shown by complexes **1** is comparable to that observed for acylrhodium complexes containing pyridine and diphenylphosphinous acid that hydrolyse AB and TBAB at 298 K with rate constants k_{obs} = (1.54 ± 0.07) × 10^{-3} and (0.95 ± 0.05) × 10^{-3} s^{-1}, respectively.[3d]

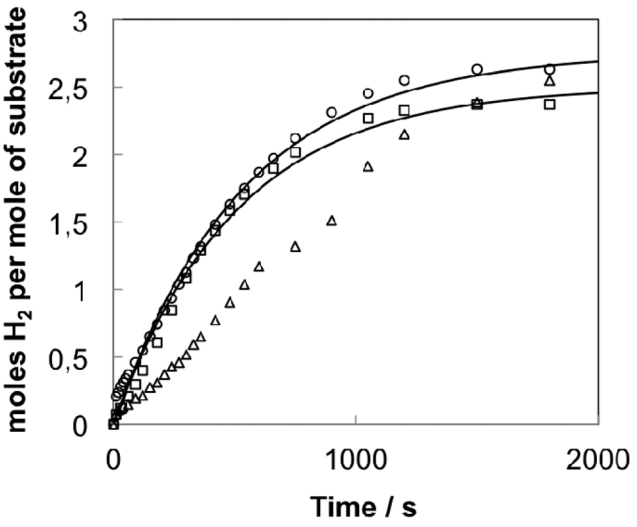


Fig. 4 Hydrogen release from AB (○), TBAB (□), or DMAB (△) as substrates, with an initial substrate concentration of 0.46 M, in the presence of 0.5 mol% of **1-Hdmpz** as the catalyst in THF/H_2O mixtures. *T*, 298 K. Open marks represent the experimental points. Solid lines represent the regression line.

Conclusions

The stereoselective formation of hydrido(acylphosphane)-(chlorido)(pyrazole)rhodium(III) complexes, with chlorido *trans* to acyl and hydrido *trans* to pyrazole and stabilized by the formation of hydrogen bonds, is accomplished. The formation of N–H···Cl and N–H···O hydrogen bonding occurs and the former is preferred to the latter. Steric hindrance lowers the stereoselectivity of the reaction by lowering the energy difference between isomers. In close agreement with the experimental NMR data, DFT calculations were able to predict the isomer/rotamer proportions and the particular intramolecular hydrogen bonds established in each case. The bis(pyrazole) complexes are efficient homogeneous catalysts for the hydrolysis of ammonia– or amine–borane adducts in air to produce hydrogen.

Experimental section

General procedures

The preparation of the metal complexes was carried out at room temperature, 298 K, under nitrogen by standard Schlenk techniques. [{RhCl(COD)}$_2$][33] and PPh_2(*o*-C_6H_4CHO)[34] were prepared as previously reported. Microanalysis was carried out with a Leco CHNS–932 microanalyser. IR spectra were recorded with a Nicolet FTIR 510 spectrophotometer in the range 4000–400 cm^{-1} using KBr pellets. NMR spectra were recorded with Bruker Avance DPX 300 or Bruker Avance 500 spectrometers. ^{1}H and ^{13}C{^{1}H} (TMS internal standard), ^{31}P{^{1}H} (H_3PO_4 external standard) NMR spectra were measured

in $CDCl_3$ solutions. The resonances of the pyrazoles were assigned by performing COSY and HSQC 2D experiments.

Preparation of [RhClH{PPh$_2$(*o*-C$_6$H$_4$CO)}(L)$_2$] (L = Hpz, 1-Hpz; Hmpz, 1-Hmpz; Hdmpz, 1-Hdmpz). To a benzene solution of [{RhCl(COD)}$_2$] (0.06 mmol) was added a stoichiometric amount (0.24 mmol) of the corresponding ligand, whereupon a yellow solid was formed. Addition of PPh$_2$(*o*-C$_6$H$_4$CHO) (0.12 mmol) and stirring at room temperature for 1 h afforded a yellow solution. Addition of hexane gave pale yellow precipitates, which were filtered off, washed with hexane and dried under vacuum. **Data for 1-Hpz**. Yield: 60%. IR (KBr, cm^{-1}): 3292 (s), ν(N–H); 2063 (s), ν(Rh–H); 1629 (s), ν(C═O). Anal. Calcd for $C_{25}H_{23}ClN_4OPRh$; C 53.16, H 4.11, N 9.92; found C 52.89, H 4.17, N 9.92. ^{1}H NMR: ($CDCl_3$): δ −15.79 (dd, 1H, J(Rh,H) = 21.0 Hz, J(P,H) = 15.4 Hz, Rh*H*); Hpz: 14.02 (s, 1H, NH···O); 11.75 (s, 1H, NH); 8.47 (s, 1H, CH); 7.64 (s, 1H, CH); 7.00 (s, 1H, CH); 6.95 (s, 1H, CH); 6.35 (s, 1H, CH); 5.85 (s, 1H, CH); phenyl: 8.23, 7.96, 7.51, 7.37, 7.20, 7.14 and 7.10 (m, 14H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 79.0 (d, J(Rh,P) = 166 Hz). **Data for 1-Hmpz**. Yield: 60%. IR (KBr, cm^{-1}): 3212 (m), ν(N–H); 2044 (m), ν(Rh–H); 1634 (m), ν(C═O). Anal. Calcd for $C_{27}H_{27}ClN_4OPRh$; C 54.70, H 4.59, N 9.45; found C 54.80, H 4.51, N 9.17. **Data for 1a-Hmpz**. ^{1}H NMR: ($CDCl_3$): δ −15.78 (dd, 1H, J(Rh,H) = 21.0 Hz, J(P,H) = 15.0 Hz, Rh*H*); Hmpz: 13.50 (s, 1H, NH···O); 11.12 (s, 1H, NH); 8.31 (s, 1H, CH); 6.88 (s, 1H, CH); 6.08 (s, 1H, CH); 5.54 (s, 1H, CH); 2.40 (s, 3H, CH_3); 1.86 (s, 3H, CH_3); phenyl: 8.24, 7.94, 7.65, 7.49, 7.23 and 7.10 (m, 14H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 79.2 (d, J(Rh,P) = 166 Hz). **Data for 1a′-Hmpz**. ^{1}H NMR: ($CDCl_3$): δ −16.27 (dd, 1H, J(Rh,H) = 21.6 Hz, J(P,H) = 15.1 Hz, Rh*H*); Hmpz: 13.88 (s, 1H, NH···O); 11.96 (s, 1H, NH); 2.42 (s, 3H, CH_3); 1.60 (s, 3H, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 79.0 (d, J(Rh,P) = 163 Hz). **Data for 1-Hdmpz**. Yield: 40%. IR (KBr, cm^{-1}): 3258 (m), ν(N–H); 2066 (m), ν(Rh–H); 1637 (s), ν(C═O). Anal. Calcd for $C_{29}H_{31}ClN_4OPRh{\cdot}0.25(C_6H_6)$; C 57.20, H 5.12, N 8.75; found C 57.76, H 4.93, N 8.37. ^{1}H NMR: ($CDCl_3$, 213 K): δ −16.14 (dd, 1H, J(Rh,H) = 30.7 Hz, J(P,H) = 14.6 Hz, Rh*H*); −15.63 (dd, 1H, J(Rh,H) = 20.9 Hz, J(P,H) = 15.3 Hz, Rh*H*); Hdmpz: 12.17 (s, 1H, NH···O); 11.17 (s, 1H, NH); 10.63 (s, H, NH); 10.55 (s, H, NH); 5.76 (s, 2H, CH); 5.56 (s, 1H, CH), 5.23 (s, 1H, CH); 2.15 (s, 3H, CH_3); 2.13 (s, 3H, CH_3); 2.02 (s, 3H, CH_3); 2.00 (s, 3H, CH_3); 1.83 (s, 3H, CH_3); 1.79 (s, 6H, CH_3); 1.33 (s, 3H, CH_3); phenyl: 8.07, 7.84, 7.77, 7.69, 7.47, 7.41 and 7.12 (m, 28H). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 77.9 (d, J(Rh,P) = 166 Hz); 77.5 (d, J(Rh,P) = 162 Hz).

Preparation of [RhCl$_2${PPh$_2$(*o*-C$_6$H$_4$CO)}(L)$_2$] (L = Hpz, 2-Hpz; Hmpz, 2-Hmpz; Hdmpz, 2-Hdmpz). A chloroform solution of the corresponding **1** (0.05 mmol) was stirred at room temperature for 48 h. Addition of hexane gave yellow precipitates, which were filtered off, washed with hexane and dried under vacuum. **Data for 2-Hpz**. Yield: 60%. IR (KBr, cm^{-1}): 3295 (s), ν(N–H); 1664 (s), ν(C═O). Anal. Calcd for $C_{25}H_{22}Cl_2N_4OPRh$; C 50.11, H 3.70, N 9.35; found C 50.34, H 3.64, N 9.05. ^{1}H NMR: ($CDCl_3$): δ Hpz: 12.73 (s, 1H, NH); 12.69 (s, 1H, NH); 8.11 (s, 1H, CH); 7.63 (s, 1H, CH); 7.03 (s, 1H, CH); 6.86 (s, 1H, CH); 6.36 (s, 1H, CH); 5.78 (s, 1H, CH); phenyl: 8.46, 7.80, 7.54, 7.50 and 7.17 (m, 14H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 59.2 (d, J(Rh, P) = 137 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 228.5 (dd, J(Rh,CO) = 28 Hz, J(P,CO) = 3 Hz, *C*═O); Hpz: 140.4 (s, CH); 132.2 (s, CH); 129.4 (s, CH); 124.8 (s, CH); 107.4 (s, CH); 106.4 (s, CH); phenyl: 139.8 (d, J = 3 Hz), 136.2 (d, J = 10 Hz), 132.6 (d, J = 7 Hz), 131.8 (d, J = 3 Hz), 131.6 (d, J = 10 Hz), 131.3 (s), 130.2 (d, J = 3 Hz), 129.2 (d, J = 3 Hz), 128.3 (d, J = 11 Hz), 128.1 (d, J = 11 Hz) (18C). **Data for 2-Hmpz**. Yield: 57%. IR (KBr, cm^{-1}): 3239 (m), 3189 (s), ν(N–H); 1662 (s), ν(C═O). Anal. Calcd for $C_{27}H_{26}Cl_2N_4OPRh$; C 51.70, H 4.18, N 8.93; found C 51.31, H 4.19, N 8.53. ^{1}H NMR: ($CDCl_3$): δ Hmpz: 12.20 (s, 1H, NH); 12.11 (s, 1H, NH); 7.83 (s, 1H, CH); 6.77 (s, 1H, CH); 6.07 (s, 1H, CH); 5.49 (s, 1H, CH); 2.35 (s, 3H, CH_3); 1.92 (s, 3H, CH_3); phenyl: 8.47, 8.08, 7.79, 7.60, 7.49, 7.20 and 7.01 (m, 14H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 58.7 (d, J(Rh,P) = 136 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 227.7 (dd, J(Rh,CO) = 28 Hz, J(P,CO) = 4 Hz, *C*═O); Hmpz: 140.8 (s, CH); 140.7 (s, CH); 106.7 (s, CH); 105.9 (s, CH); 11.2 (s, CH_3); 10.9 (s, CH_3); phenyl: 140.3 (s), 136.2 (d, J = 10 Hz), 132.4 (d, J = 6 Hz), 132.4 (s), 132.0 (s), 131.6 (d, J = 9 Hz), 131.2 (s), 129.9 (d, J = 3 Hz), 128.2 (d, J = 11 Hz), 127.7 (d, J = 11 Hz) (18C). **Data for 2-Hdmpz**. Yield: 59%. IR (KBr, cm^{-1}): 3371 (s), ν(N–H); 1673 (s), ν(C═O). Anal. Calcd for $C_{29}H_{30}Cl_2N_4OPRh{\cdot}0.25(CHCl_3)$; C 51.27, H 4.45, N 8.17; found C 51.31, H 4.36, N 8.31. ^{1}H NMR: ($CDCl_3$): δ Hdmpz: 12.63 (s, 1H, NH); 11.14 (s, 1H, NH); 5.80 (s, 1H, CH); 5.27 (s, 1H, CH); 2.25 (s, 3H, CH_3); 2.09 (s, 3H, CH_3); 1.66 (s, 3H, CH_3); 1.31 (s, 3H, CH_3); phenyl: 8.09, 7.92, 7.67, 7.48, 7.39 and 7.11(m, 14H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 57.4 (d, J(Rh,P) = 137 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 221.8 (dd, J(Rh,CO) = 27 Hz, J(P,CO) = 3 Hz, *C*═O); Hdmpz: 107.3 (s, CH); 106.4 (s, CH); 14.4 (s, CH_3); 11.8 (s, CH_3); 11.1 (s, CH_3); 10.8 (s, CH_3); phenyl: 140.5 (s), 139.6 (s), 135.3 (d, J = 9 Hz), 132.7 (s), 32.5 (s), 131.9 (d, J = 9 Hz), 131.7 (d, J = 6 Hz), 131.1 (d, J = 3 Hz), 130.3 (d, J = 3 Hz), 128.0 (d, J = 10 Hz), 127.9 (d, J = 11 Hz), 125.2 (d, J = 16 Hz) (18C).

Preparation of [RhHCl{PPh$_2$(*o*-C$_6$H$_4$CO)}(PPh$_3$)L] (L = Hpz, 3-Hpz; Hmpz, 3-Hmpz; Hdmpz, 3-Hdmpz). To a dichloromethane solution of the corresponding **1** (0.05 mmol) was added a slight excess (0.06 mmol) of triphenylphosphane. Stirring for 1 h at room temperature afforded a yellow solution. Addition of hexane gave yellow precipitates, which were filtered off, washed with hexane and dried under vacuum. **Data for 3-Hpz**. Yield: 42%. IR (KBr, cm^{-1}): 3231 (s), ν(N–H); 2046 (m), ν(Rh–H); 1621 (s), ν(C═O). Anal. Calcd for $C_{40}H_{34}N_2OP_2Rh{\cdot}0.25(CH_2Cl_2)$; C 61.96, H 4.46, N 3.59; found C 62.28, H 4.21, N 3.67. ^{1}H NMR ($CDCl_3$): δ −14.05 (ddd, 1H, J(Rh,H) = 17.1 Hz, J(P,H) = 11.9, 4.0 Hz, Rh*H*); Hpz: 11.80 (s, 1H, N*H*); 6.69 (s, 1H, C*H*); 6.60 (s, 1H, C*H*); 5.54 (s, 1H, C*H*); phenyl: 8.31, 7.72, 7.58, 7.46, 7.42, 7.24, 7.10 and 7.00 (m, 29H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 62.3 (dd, J(P,P) = 377 Hz, J(Rh,P) = 138 Hz, *P*Ph$_2$(*o*-C$_6$H$_4$CO)); 44.2 (dd, J(Rh,P) = 124 Hz, *P*Ph$_3$P). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 234.9 (d, J(Rh,C) = 32 Hz, *C*═O); Hpz: 138.5 (s, *C*H); 129.1 (s, *C*H); 105.4 (s, *C*H); phenyl: 135.4 (d, J = 12 Hz), 134.2 (d, J = 11 Hz), 131.6 (d, J = 10 Hz), 131.3 (d, J = 5 Hz), 131.1 (d, J = 6 Hz), 130.8 (d, J = 4 Hz), 128.7 (d, J = 11 Hz), 126.7 (s) and 122.5 (d, J = 17 Hz) (36C). **Data for**

3-Hmpz. Yield: 58%. IR (KBr, cm^{-1}): 3242 (s), ν(N–H); 2036 (m), ν(Rh–H); 1623 (s), ν(C═O). Anal. Calcd for $C_{41}H_{36}N_2OP_2Rh$; C 63.70, H 4.69, N 3.62; found C 64.11, H 4.70, N 3.68. ^{1}H NMR ($CDCl_3$): δ −14.02 (ddd, 1H, J(Rh,H) = 19.0 Hz, J(P,H) = 12.3 Hz, 4.6 Hz, Rh*H*); Hmpz: 11.25 (s, 1H, NH); 6.41 (s, 1H, CH); 5.25 (s, 1H, CH); 1.75 (s, 3H, CH_3); phenyl: 8.32, 7.74, 7.58, 7.46, 7.41, 7.23, 7.13, 7.05 and 7.00 (m, 29H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 62.6 (dd, J(P,P) = 379 Hz, J(Rh,P) = 137 Hz, PPh_2(*o*-C_6H_4CO)); 44.4 (dd, J(Rh,P) = 124 Hz, *P*h_3P). ^{13}C{^{1}H} NMR ($CDCl_3$, 303 K): δ 235.0 (d, J(Rh,C) = 35 Hz, *C*═O); Hmpz: 139.1 (s, *C*H); 129.1 (s, *C*–CH_3); 104.7 (s, *C*H); 10.7 (s, *C*H_3); phenyl: 137.4 (s), 135.5 (d, J = 12 Hz), 134.3 (d, J = 11 Hz), 133.9 (s), 133.5 (s), 131.8 (d, J = 10 Hz), 131.3 (d, J = 5 Hz), 131.1 (d, J = 6 Hz), 130.8 (d, J = 4 Hz), 128.7 (d, J = 11 Hz) and 127.6 (d, J = 10 Hz) (36C). **Data for 3-Hdmpz**. Yield: 58%. IR (KBr, cm^{-1}): 3219 (s), ν(N–H); 2053 (m), ν(Rh–H); 1631 (s), ν(C═O). Anal. Calcd for $C_{42}H_{38}ClN_2OP_2Rh$; C 64.09, H 4.87, N 3.56; found C 63.92, H 4.32, N 3.80. ^{1}H NMR ($CDCl_3$): δ −14.73 (m, 1H, Rh*H*); −14.51 (dt, 1H, J(Rh,H) = 27.3 Hz, J(P,H) = 7.7 Hz, Rh*H*); Hdmpz: 11.50 (s, 1H, N*H*); 11.03 (s, 1H, N*H*); 5.35 (s, 1H, CH); 5.08 (s, 1H, CH); 1.79 (s, 3H, CH_3); 1.72 (s, 3H, CH_3); 1.48 (s, 3H, CH_3); 0.98 (s, 3H, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 65.1 (dd, J(P,P) = 379 Hz, J(Rh,P) = 133 Hz, PPh_2(*o*-C_6H_4CO); 37.9 (dd, J(Rh,P) = 127 Hz, *P*h_3P) and δ 63.8 (dd, J(P,P) = 376 Hz, J(Rh,P) = 140 Hz, PPh_2(*o*-C_6H_4CO)); 41.3 (dd, J(Rh,P) = 124 Hz, *P*h_3P). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 233.9 (d, J(Rh,C) = 28 Hz, *C*═O); 232.0 (d, J(Rh,C) = 35 Hz, *C*═O); Hdmpz: 129.8 (s, *C*–CH_3); 129.1 (s, *C*–CH_3); 105.8 (s, CH); 105.3 (s, CH); 13.7 (s, CH_3); 13.3 (s, CH_3); 10.7 (s, CH_3); 10.6 (s, CH_3).

Preparation of [RhHCl{PPh_2(*o*-C_6H_4CO)}(PPh_2OH)L] (L = Hpz, 4-Hpz; Hmpz, 4-Hmpz; Hdmpz, 4-Hdmpz). To a benzene solution of the corresponding **1** (0.05 mmol) was added diphenylphosphane oxide (0.055 mmol). After stirring for 1 h under reflux at 80 °C, the addition of hexane gave yellow precipitates, which were filtered off, washed with hexane and dried under vacuum. **Data for 4-Hpz**. Yield: 54%. IR (KBr, cm^{-1}): 3260(m), ν(N–H); 2072 (m), ν(Rh–H); 1625 (m), ν(C═O). Anal. Calcd for $C_{34}H_{30}ClN_2O_2P_2Rh$; C 58.43, H 4.33, N 4.01; found C 57.99, H 4.89, N 4.46. ^{1}H NMR ($CDCl_3$): δ −14.20 (dt, 1H, J(Rh,H) = 19.8 Hz, J(P,H) = 9.5 Hz, Rh*H*); Hpz: 12.00 (s, 1H, PPh_2P(O)*H*); 10.99 (s, 1H, NH); 6.82 (s, 1H, CH); 6.62 (s, 1H, CH); 5.77 (s, 1H, CH); phenyl: 8.21, 7.93, 7.68, 7.52, 7.44, 7.31, 7.12 and 7.02 (m, 24H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 98.4 (dd, J(P,P) = 419 Hz, J(Rh,P) = 126 Hz, *P*h_2P(O)H); 60.6 (dd, J(Rh,P) = 120 Hz, *P*PPh_2(*o*-C_6H_4CO)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 246.8 (d, J(Rh,C) = 37 Hz, *C*═O); Hpz: 138.7 (s, CH); 127.6 (s, CH); 106.0 (s, CH); phenyl: 135.2 (d, J = 13 Hz), 132.6 (d, J = 14 Hz), 131.6 (d, J = 10 Hz), 131.5 (d, J = 4 Hz), 131.4 (s), 131.2 (s), 130.5 (s), 130.4 (s), 129.3 (s), 128.9 (s), 128.8 (s), 128.0 (d, J = 11 Hz), 127.8 (d, J = 10 Hz), 127.0 (d, J = 10 Hz), 123.6 (d, J = 17 Hz) (30C). **Data for 4-Hmpz**. Yield: 58%. IR (KBr, cm^{-1}): 3260 (m), ν(N–H); 2018 (m), ν(Rh–H); 1626 (m), ν(C═O). Anal. Calcd for $C_{35}H_{32}ClN_2O_2P_2Rh$; C 58.96, H 4.52, N 3.93; found C 58.85, H 4.25, N 4.42. **Data for 4a-Hmpz**. ^{1}H NMR: ($CDCl_3$): δ −14.20 (dt, 1H, J(Rh,H) = 19.7 Hz, J(P,H) = 9.5 Hz, Rh*H*); Hmpz: 12.11 (s, 1H, PPh_2P(O)*H*); 10.42 (s, 1H, NH); 6.62 (s, 1H, CH); 5.46 (s, 1H, CH); 1.62 (s, 3H, CH_3); phenyl: 8.21, 7.92, 7.68, 7.52, 7.44, 7.36, 7.13 and 7.04 (m, 24H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 98.4 (dd, J(P,P) = 423 Hz, J(Rh,P) = 126 Hz, *P*h_2P(O)H); 60.8 (dd, J(Rh,P) = 120 Hz, *P*PPh_2(*o*-C_6H_4CO)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 247.0 (d, J(Rh,C) = 37 Hz, *C*═O); Hmpz: 139.2 (s, CH); 129.2 (s, *C*–CH_3); 105.5 (s, CH); 10.6 (s, CH_3); phenyl: 138.6 (s), 135.2 (d, J = 13 Hz), 132.7 (d, J = 14 Hz), 132.5 (d, J = 5 Hz), 131.8 (d, J = 10 Hz), 131.5 (d, J = 4 Hz), 131.4 (s), 131.2 (s), 130.7 (s), 130.6 (d, J = 5 Hz), 128.8 (s), 128.7 (s), 128.0 (d, J = 11 Hz), 127.6 (d, J = 9 Hz), 126.8 (d, J = 10 Hz), 123.5 (d, J = 16 Hz) (30C). **Data for 4a′-Hmpz**. ^{1}H NMR: ($CDCl_3$): δ −14.57 (m, 1H, Rh*H*); 12.22 (s, 1H, PPh_2P(O)*H*); Hmpz: 11.16 (s, 1H, NH); 6.44 (s, 1H, CH); 5.41 (s, 1H, CH); 1.56 (s, 3H, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 98.8 (dd, J(P,P) = 419 Hz, J(Rh,P) = 125 Hz, *P*h_2-P(O)H); 60.6 (dd, J(Rh,P) = 121 Hz, *P*PPh_2(*o*-C_6H_4CO)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.9 (s, CH); Hmpz: 129.4 (s, *C*–CH_3); 105.9 (s, CH); 10.9 (s, CH_3). **Data for 4-Hdmpz**. Yield: 53%. IR (KBr, cm^{-1}): 3242 (m), ν(N–H); 2033 (m), ν(Rh–H); 1624 (m), ν(C═O). Anal. Calcd for $C_{36}H_{34}ClN_2O_2P_2Rh$; C 59.48, H 4.71, N 3.85; found C 59.39, H 4.67, N 4.02. ^{1}H NMR ($CDCl_3$): δ −14.53 (dt, 1H, J(Rh,H) = 19.3 Hz, J(P,H) = 8.6 Hz, Rh*H*); Hdmpz: 12.68 (s, 1H, PPh_2P(O)*H*); 10.67 (s, 1H, NH); 5.12 (s, 1H, CH); 1.55 (s, 3H, CH_3); 1.46 (s, 3H, CH_3); phenyl: 8.21, 8.15, 7.94, 7.72, 7.46, 7.17 and 7.08 (m, 24H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 98.9 (dd, J(P,P) = 422 Hz, J(Rh,P) = 126 Hz, *P*h_2-P(O)H); 60.7 (dd, J(Rh,P) = 120 Hz, *P*PPh_2(*o*-C_6H_4CO)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 246.0 (d, J(Rh,C) = 38 Hz, *C*═O); Hdmpz: 105.5 (s, CH); 13.4 (s, CH_3); 10.4 (s, CH_3); phenyl: 138.2 (s), 135.0 (d, J = 13 Hz), 132.8 (d, J = 14 Hz), 132.2 (d, J = 5 Hz), 131.8 (s), 131.8 (d, J = 10 Hz), 131.6 (d, J = 4 Hz), 131.4 (s), 131.0 (s), 130.4 (s), 130.3 (s), 129.2 (s), 128.7 (s), 128.6 (s), 127.9 (d, J = 11 Hz), 127.5 (d, J = 10 Hz), 126.8 (d, J = 10 Hz), 123.5 (d, J = 16 Hz) (30C).

Preparation of [RhHCl{PPh_2(*o*-C_6H_4CO)}{PPh_2(*o*-C_6H_4CHO)-κ*P*}L] (L = Hpz, 5-Hpz; Hdmpz, 5-Hdmpz). To a benzene solution of [{RhCl(COD)}$_2$] (0.06 mmol) was added a stoichiometric amount (0.12 mmol) of the corresponding ligand, whereupon a yellow solid was formed. Addition of PPh_2(*o*-C_6H_4CHO) (0.30 mmol) and stirring at room temperature for 1 h followed by addition of hexane gave pale yellow precipitates, which were filtered off, washed with hexane and dried under vacuum. **Data for 5-Hpz**. Yield: 45%. IR (KBr, cm^{-1}): 3234 (s), ν(N–H); 2043 (m), ν(Rh–H); 1687 (s), ν(HC═O); 1622 (s), ν(C═O). Anal. Calcd for $C_{41}H_{34}N_2O_2P_2Rh$; C 62.57, H 4.35, N 3.56; found C 62.81, H 4.47, N 3.43. ^{1}H NMR ($CDCl_3$): δ −14.10 (ddd, 1H, J(Rh,H) = 17.2 Hz, J(P,H) = 12.1 Hz, 4.0 Hz, Rh*H*); Hpz: 11.63 (s, 1H, NH); 10.27 (s, 1H, *H*–CO); 6.72 (s, 1H, CH); 6.57 (s, 1H, CH); 5.60 (s, 1H, CH); phenyl: 8.34, 7.70, 7.58, 7.47, 7.29, 7.22 and 7.13 (m, 28H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 65.4 (dd, J(P,P) = 370 Hz, J(Rh,P) = 141 Hz, PPh_2(*o*-C_6H_4CO)); 40.2 (dd, J(Rh,P) = 123 Hz, PPh_2(*o*-C_6H_4CHO)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 234.5 (d, J(Rh,C) = 31 Hz, *C*═O); 191.7 (s, H*C*═O); Hpz: 138.8 (s, CH); 127.8 (s, CH); 105.9 (s, CH); phenyl: 138.1 (d, J = 7 Hz), 135.5 (d, J = 13 Hz), 135.4 (d, J = 5 Hz), 134.9 (d, J = 13 Hz), 134.5 (d, J = 12 Hz), 132.3 (d, J = 7 Hz), 131.6 (s), 131.3 (s), 130.8 (d,

J = 4 Hz), 129.9 (s), 129.5 (s), 129.3 (s), 128.8 (d, J = 11 Hz), 128.3 (d, J = 10 Hz), 128.1 (d, J = 10 Hz), 127.9 (d, J = 10 Hz), 122.7 (d, J = 17 Hz) (36C). **Data for 5-Hdmpz**. Yield: 60%. IR (KBr, cm^{-1}): 3202 (s), ν(N–H); 2057 (m), ν(Rh–H); 1687 (s), ν(HC═O); 1626, ν(C═O). Anal. Calcd for $C_{43}H_{38}N_2O_2P_2Rh$; C 63.36, H 4.70, N 3.44; found C 63.22, H 4.97, N 3.27. **Data for 5a-Hdmpz**. ^{1}H NMR ($CDCl_3$): δ −14.74 (m, 1H, Rh*H*); 11.41 (s, 1H, N*H*); Hdmpz: 10.26 (s, 1H, *H*–CO); 5.15 (s, 1H, CH); 1.68 (s, 3H, CH_3); 0.96 (s, 3H, CH_3); phenyl: 8.30, 7.97, 7.82, 7.74, 7.64, 7.56, 7.44, 7.31, 7.12 and 7.06 (m, 28H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 66.6 (dd, J(P,P) = 369 Hz, J(Rh,P) = 142 Hz, *P*Ph_2-(o-C_6H_4CO)); 36.8 (dd, J(Rh,P) = 124 Hz, *P*Ph_2(o-C_6H_4CHO)). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 231.5 (d, J(Rh,C) = 32 Hz, *C*═O); 190.4 (s, H*C*═O); Hdmpz: 106.3 (s, CH); 12.7 (s, CH_3); 10.6 (s, CH_3). **Data for 5b-Hdmpz**. ^{1}H NMR ($CDCl_3$): δ −14.37 (ddd, 1H, J(Rh, H) = 26.0 Hz, J(P,H) = 10.4 Hz, J(P,H) = 5.8 Hz, Rh*H*); Hdmpz: 11.08 (s, 1H, N*H*); 9.91 (s, 1H, *H*–CO); 5.34 (s, 1H, CH); 1.83 (s, 3H, CH_3); 1.16 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 65.8 (dd, J(P,P) = 375 Hz, J(Rh,P) = 137 Hz, *P*Ph_2(o-C_6H_4CO)); 35.9 (dd, J(Rh,P) = 127 Hz, *P*Ph_2(o-C_6H_4CHO)). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 229.2 (d, J(Rh,C) = 37 Hz, *C*═O); 190.0 (s, H*C*═O); Hdmpz: 105.3 (s, CH); 12.9 (s, CH_3); 10.7 (s, CH_3).

Preparation of [RhCl{PPh_2(o-C_6H_4CO)}{PPh_2(o-C_6H_4CHOH)}-(Hmpz)] (6). To a benzene solution of [{RhCl(COD)}$_2$] (0.06 mmol) was added a stoichiometric amount (0.12 mmol) of the corresponding ligand, whereupon a yellow solid was formed. Addition of PPh_2(o-C_6H_4CHO) (0.30 mmol) and stirring for 5 min under reflux at 80 °C, afforded a yellow solution. Addition of hexane gave pale yellow precipitates, which were filtered off, washed with hexane and dried under vacuum. Yield: 40%. IR (KBr, cm^{-1}): 3205 (m), ν(N–H); 1633 (s), ν(C═O). Anal. Calcd for $C_{42}H_{35}N_2O_2P_2Rh$; C 62.97, H 4.53, N 3.50; found C 62.37, H 4.41, N 3.91. **Data for 6a**. ^{1}H NMR ($CDCl_3$): δ Hmpz: 12.09 (s, 1H, N*H*); 6.51 (s, 1H, CH); 5.59 (s, 1H, CH); 1.94 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 55.2 (dd, J(P,P) = 19 Hz, J(Rh,P) = 152 Hz, *P*Ph_2-(o-C_6H_4CHOH)); 29.3 (dd, J(Rh,P) = 83 Hz, *P*Ph_2(o-C_6H_4CO)). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 239.8 (dd, J(Rh,C) = 35 Hz, J(P,C) = 9 Hz, *C*═O); 90.6 (dd, J(Rh,C) = 22 Hz, J(P,C) = 103 Hz, *C*HOH); 10.9 (s, CH_3). **Data for 6b**. ^{1}H NMR ($CDCl_3$): δ Hmpz: 11.49 (s, 1H, N*H*); 6.09 (s, 1H, CH); 5.69 (s, 1H, CH); 1.87 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 55.5 (dd, J(P,P) = 16 Hz, J(Rh,P) = 168 Hz, *P*Ph_2(o-C_6H_4CHOH)); 32.5 (dd, J(Rh,P) = 87 Hz, *P*Ph_2(o-C_6H_4CO)). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 229.9 (d, J(Rh,C) = 33 Hz, *C*═O); 94.2 (dd, J(Rh,C) = 22 Hz, J(P,C) = 99 Hz, *C*HOH); 11.0 (s, CH_3).

Preparation of [RhCl{PPh_2(o-C_6H_4CO)}$_2$L] (L = Hpz, 7-Hpz; Hmpz, 7-Hmpz; Hdmpz, 7-Hdmpz). To a benzene solution of [{RhCl(COD)}$_2$] (0.06 mmol) was added a stoichiometric amount (0.12 mmol) of the corresponding ligand, whereupon a yellow solid was formed. Addition of PPh_2(o-C_6H_4CHO) (0.30 mmol) and stirring for 90 min under reflux at 80 °C, afforded a yellow solution. Addition of hexane gave pale yellow precipitates, which were filtered off, washed with hexane and dried under vacuum. Complex **7-Hmpz** was recrystallized from dichloromethane/diethyl ether. **Data for 7-Hpz**. Yield: 73%. IR (KBr, cm^{-1}): 3225 (s), ν(N–H); 1641 (s), 1624 (s), ν(C═O). Anal. Calcd for $C_{41}H_{32}N_2O_2P_2Rh{\cdot}0.25(C_6H_6)$; C 63.45, H 4.20, N 3.48; found C 63.40, H 4.34, N 3.95. ^{1}H NMR ($CDCl_3$): δ Hpz: 11.48 (s, 1H, N*H*); 7.08 (s, 1H, CH); 6.85 (s, 1H, CH); 5.86 (s, 1H, CH); phenyl: 8.17, 7.93, 7.71, 7.62, 7.49, 7.35, 7.25 and 7.05 (m, 28H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 61.0 (dd, J(P,P) = 337 Hz, J(Rh,P) = 150 Hz, *P*Ph_2(o-C_6H_4CO)); 51.5 (dd, J(Rh,P) = 138 Hz, *P*Ph_2(o-C_6H_4CO)). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 233.5 (d, br, J(Rh, C) = 33 Hz, *C*═O); Hpz: 139.7 (s, CH); 127.4 (s, CH); 106.1 (s, CH); phenyl: 136.9 (d, J = 11 Hz), 133.7 (d, J = 10 Hz), 133.4 (d, J = 10 Hz), 132.0 (s), 131.5 (s), 131.2 (d, J = 7 Hz), 130.9 (s), 130.7 (s), 129.8 (d, J = 11 Hz), 129.0–127.7 (m), 127.5 (s), 123.9 (d, J = 7 Hz) and 123.8 (d, J = 6 Hz) (36C). **Data for 7-Hmpz**. Yield: 62%. IR (KBr, cm^{-1}): 3216 (s), ν(N–H); 1642 (s), 1621 (s), ν(C═O). Anal. Calcd for $C_{42}H_{34}N_2O_2P_2Rh{\cdot}0.5(CH_2Cl_2)$; C, 60.66, H, 4.19, N, 3.33; found C 60.59, H 4.44, N 3.37. ^{1}H NMR ($CDCl_3$): δ Hmpz: 10.92 (s, 1H, N*H*); 6.88 (s, 1H, CH); 5.55 (s, 1H, CH); 1.81 (s, 3H, CH_3); phenyl: 8.15, 7.92, 7.69, 7.58, 7.47, 7.27 and 7.01 (m, 28H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.9 (dd, J(P,P) = 340 Hz, J(Rh,P) = 152 Hz, *P*Ph_2(o-C_6H_4CO)); 51.4 (dd, J(Rh,P) = 139 Hz, *P*Ph_2(o-C_6H_4CO)). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 233.6 (d, J(Rh,C) = 33 Hz, C═O); 232.8 (d, J(Rh,C) = 36 Hz, C═O); Hmpz: 140.4 (s, CH); 105.5 (s, CH); 10.7 (s, CH_3); phenyl: 136.9 (d, J = 10 Hz), 133.8 (d, J = 10 Hz), 133.5 (d, J = 10 Hz), 132.5 (s), 132.3–131.9 (m), 131.7 (d, J = 5. Hz), 131.5 (s), 131.4 (s), 131.3 (s), 130.9 (d, J = 12 Hz), 129.9 (s), 129.7 (s), 129.2–128.4 (m), 128.1 (d, J = 10 Hz), 127.8 (d, J = 10 Hz), 127.4 (d, J = 10 Hz), 124.1 (d, J = 19 Hz) and 123.1 (d, J = 18 Hz) (36C). **Data for 7-Hdmpz**. Yield: 92%. IR (KBr, cm^{-1}): 3194 (m), ν(N–H); 1642 (s), 1623 (s), ν(C═O). Anal. Calcd for $C_{43}H_{36}N_2O_2P_2Rh$; C 63.52, H 4.46, N 3.44; found C 62.70, H 4.24, N 3.53. ^{1}H NMR ($CDCl_3$): δ Hdmpz: 11.16 (s, 1H, N*H*); 5.41 (s, 1H, CH); 1.80 (s, 3H, CH_3); 1.39 (s, 3H, CH_3); phenyl: 8.09, 7.88, 7.67, 7.59, 7.47, 7.34, 7.21, 7.13, 6.97 and 6.83 (m, 28H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 58.3 (dd, J(P,P) = 340 Hz, J(Rh,P) = 155 Hz, *P*Ph_2(o-C_6H_4CO)); 52.9 (dd, J(Rh,P) = 143 Hz, *P*Ph_2(o-C_6H_4CO)). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 229.3 (d, (Rh,C) = 34 Hz, *C*═O); 227.4 (d, J(Rh,C) = 36 Hz, *C*═O); Hdmpz: 106.3 (s, CH); 13.7 (s, CH_3); 10.6 (s, CH_3); phenyl: 136.2–135.4 (m), 133.7 (s), 133.5 (d, J = 9 Hz), 133.2 (s), 132.4 (d, J = 9 Hz), 132.2–131.2 (m), 130.3 (d, J = 11 Hz), 129.8 (s), 129.4, 129.1–128.3 (m), 127.8 (d, J = 9.2 Hz), 127.2 (d, J = 6.1 Hz), 125.2 (d, J = 15 Hz) and 125.0 (d, J = 16 Hz) (36C).

Crystallographic refinement and structure solution

X-ray quality crystals were obtained by vapour diffusion of diethyl ether onto dichloromethane (**2-Hpz** and **7-Hpz**,) or chloroform (**3a-Hdmpz**) solutions at −20 °C. Single crystals of suitable dimensions were used for data collection. For compounds **2-Hpz** and **3a-Hdmpz**, diffraction intensities were collected on an Agilent Technologies Super-Nova diffractometer, which was equipped with monochromated Mo Kα radiation (λ = 0.71 073 Å) and an Eos CCD detector at 100 K. For compound **7-Hpz**, intensity data were collected on a Bruker AXS APEX CCD area detector equipped with graphite monochromated Mo Kα radiation (λ = 0.71 073 Å) by applying the ω-scan

method. The structures were solved by direct methods and refined with full-matrix least-squares calculations on F^2 using the program SHELXL-97.[35] Anisotropic temperature factors were assigned to all atoms except for hydrogen atoms, which ride their parent atoms with an isotropic temperature factor arbitrarily chosen as 1.2 times that of the respective parent. Hydrogens from nitrogen atoms pertaining to pyrazole rings were located and not fixed. Attempts to solve disorder problems with the crystallization molecule failed in compound **2Hpz**. Instead, a new set of F^2 (hkl) values with the contribution from solvent molecules withdrawn was obtained by the SQUEEZE procedure implemented in PLATON-94.[36] Final $R(F)$, w$R(F^2)$ and goodness of fit agreement factors, details of the data collection and analysis can be found in Table SI-3.† CCDC reference numbers for the structures of **2-Hpz**, **3a-Hdmpz**, and **7-Hpz** are 1062495, 1062496 and 1062497, respectively.

DFT calculations

Quantum chemical calculations were carried out with the Gaussian 09 series of programs.[37] Full geometry optimizations of each species were performed in the gas phase by employing the hybrid density functional B3LYP[38] with the 6-31G(d,p) basis set for nonmetal atoms together with the LANL2DZ[39] for the metal. When available, X-ray structures were used as starting geometries. Energy values were then refined by single-point calculations on the B3LYP/LANL2DZ geometries at the M062X/6-311++G(2d,2p) level of theory and solvent (benzene) contributions to free energy were considered by means of polarizable continuum model[40] (PCM) calculations. The nature of the stationary points was verified by analytical computations of harmonic vibrational frequencies at the M062X/6-311++G(2d,2p) level of theory. A pressure of 1 atm and a temperature of 298.15 K were assumed in the calculations. The theoretical ratio of the isomers/rotamers present in solution was predicted assuming a Boltzmann distribution.[41]

Dehydrogenation of RR′R″N–BH_3 with complexes 1 or 4

A typical dehydrogenation experiment is described here for the hydrolysis of H_3N–BH_3 using 2.70 ml of THF/H_2O = 1 : 1 mixtures and 0.5 mol% catalyst loading: a solution of 38.8 mg (1.25 mmol) of H_3N–BH_3 in H_2O was prepared in a round bottom 40 ml flask fitted with a gas outlet and with a side arm sealed with a tight-fitting septum cap. The flask was connected *via* the gas outlet to a water-filled gas burette. A solution of 0.006 mmol of the corresponding catalyst in dry THF was then syringed through the septum, magnetic stirring was connected and timing started. Gas evolution began immediately and the amount of gas evolved was determined periodically by measuring the displacement of water in the burette. Volumes were measured at atmospheric pressure and 298 K.

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