Hydrido{(acylphosphine)(diphenylphosphinous acid)}rhodium(III) Complexes. Catalysts for the Homogeneous Hydrolysis of Ammoniaor Amine-Boranes under Air

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S Supporting Information

ABSTRACT: The reaction of $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) with $PPh_2(o-C_6H_4CHO)$ (Rh/P = 1:1) in the presence of 4-methylpyridine (4-pic) or isoquinoline (iquin) leads to hydridoacyl complexes [RhHCl(PPh₂(o-C₆H₄CO))L₂] (L = 4-pic, 1; iquin, 2). Their reaction with diphenylphosphine oxide affords neutral complexes [RhHCl{(PPh₂(o-C₆H₄CO))(PPh₂O)H}L] (L = pyridine (py), 4; 4-pic, 5; iquin, 6) with trans P-ligands belonging to a formally PCP pincer ligand due to the formation of a O---H---O hydrogen bond between the oxygen atom of the diphenylphosphinous acid and the oxygen atom of the coordinated acyl. The reaction of 4 with chelating N-donors (LL) leads to displacement of pyridine and chloride to afford cationic [RhH{(PPh₂(o-C₆H₄CO))(PPh₂O)H}(LL)]BPh₄ (LL = 2,2'-bipyridine, 7; biacetyldihydrazone, 8; biacetyloximehydrazone, 9; 2-aminomethylpyridine, 10), which undergo cleavage of the O---H---O hydrogen bond in solution. Complex 9, containing a nonsymmetric ligand, exists in solution as an equimolar mixture of two



isomers in equilibrium leading to fluxional behavior for which $\Delta G^{\ddagger} = 52 \pm 1$ kJ mol⁻¹ has been determined using the Eyring equation. The complexes were fully characterized spectroscopically. Single crystal X-ray diffraction analysis was performed on 8. Complexes 1-10 have been tested as homogeneous catalysts for the hydrolysis of amine- or ammonia-borane (AB) to generate up to 3 equiv of hydrogen in the presence of air. When using 0.5 mol % loading of 5, at 40 °C, complete hydrogen release from 0.46 M solutions of AB, TBAB (tert-butylamine-borane), and DMAB (dimethylamine-borane) requires 12.5, 9, or 15 min, respectively. The catalyst maintains its activity in consecutive runs. Kinetic studies indicate a first-order behavior in substrate in every case. The catalytic hydrolysis of AB shows first-order dependence on the catalyst concentration.

INTRODUCTION

Secondary phosphine oxides (SPOs), R¹R²P(O)H, exist as two tautomeric isomers in equilibrium, the pentavalent form, $R^{1}R^{2}P(=O)H$, and the trivalent phosphinous acid form, R¹R²P-OH. For simple aromatic and aliphatic substituents the equilibrium favors the pentavalent form and metal atoms may assist the tautomerization to allow the P-coordination of the trivalent form.¹ SPOs have been used as ligands for the synthesis of versatile catalysts for a variety of reactions, such as hydrophosphinylation,² hydroformylation,³ cross-coupling,⁴ nitrile hydration,⁵ or asymmetric hydrogenation⁶ reactions. Recently SPOs have been reported as useful reagents for nanoparticle stabilization.⁷ The electronic and steric effects governing the coordination preferences of SPOs have been evaluated⁸ and related to the formation of intra- or intermolecular hydrogen bond interactions. Whenever two ligands are in a *cis*-position about the metal center, they may afford the (phosphinous acid/phosphinite) moiety R¹R²PO-H----OPR¹R² with a strong intramolecular hydrogen bond.⁹ The fluxional behavior of acetyldiphenylphosphinous platinum complexes has been attributed to the formation of an

intramolecular hydrogen bond between the phosphinous acid and the acyl fragments.^{3a} Intermolecular O-H---Cl or O-H---O hydrogen bonding interactions are responsible for the formation of $[Ph_2P(\tilde{O})HAuCl]_2$ dimers¹⁰ or of infinite onedimensional chains in [Pt(CCBu^t){(PPh₂O)₂H}(PPh₂OH)], respectively.¹¹ Intermolecular hydrogen bonds between the phosphinous acid fragment and chloride or O-containing counterions have also been observed.¹²

Hydrogen is a feasible alternative to fossil fuels, but its safe storage and delivery still remains a challenge.¹³ Ammoniaborane (AB), a chemical hydrogen storage material with high hydrogen contents (H₃N-BH₃, 19.6 wt %), is considered a potential hydrogen source for portable fuel cells.¹⁴ The catalyzed dehydrogenation of ammonia- or amine-boranes for efficient hydrogen production, promoted by transition-metal catalysts under mild reaction conditions, is the subject of recent intensive research. The homogeneous dehydrocoupling catalyzed by complexes of Ti or $Zr_{,}^{15a-e}$ Cr $,^{15f}$ Fe or Ru $,^{15g-i}$

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Rh,^{15j,k} or Pd or Pt^{15l,m} may afford up to one equivalent of hydrogen gas, usually under inert atmosphere.¹⁶ Cationic Pd complexes,¹⁷ a carbene-Ni species,¹⁸ or Ru-PN complexes¹⁹ release two or more equivalents of H₂, and a boron-pendant Ru complex has been reported to efficiently afford up to two equivalents of H₂ from AB under air.²⁰ Hydrolysis reactions provide an additional method of H₂ release from ammonia- or amine-boranes and can afford up to three equivalents of hydrogen per equivalent of amine-borane adduct. Transition metal heterogeneous systems, which often require inert atmosphere, allow fast H₂ release from these amine-borane adducts at room temperature,²¹ and rhodium nanoparticles are among the most effective catalysts for this hydrolysis reaction.²² The efficient homogeneously catalyzed version of this reaction has been reported more recently using the complexes shown in Chart 1: hydridoirida- β -diketones (i),²³ Ir-PNP complexes

Chart 1



(ii),²⁴ coordinatively unsaturated Ir-carbene derivatives (iii),²⁵ dicarbonylruthenacyclic compounds (iv),²⁶ or Ru-bipyridine-*p*-cymene complexes (v).²⁷

Hydridoirida- β -diketones contain an acyl and a hydroxycarbene group, are stabilized by a strong O---H---O intramolecular hydrogen bond,²⁸ and are efficient and robust homogeneous catalysts for the hydrolysis of AB in air. Because rhodium nanoparticles are among the most effective heterogeneous catalysts for this hydrolytic reaction,²² we thought it interesting to prepare hydridoacylrhodium(III) complexes containing an O---H---O intramolecular hydrogen bond that could also behave as efficient catalysts. A variety of hydridoacylrhodium(III) complexes are known,²⁹ though no hydridorhoda- β -diketone has yet been obtained. We reasoned that the reaction of acyl complexes with diphenylphosphine oxide would afford new derivatives containing the desired intramolecular hydrogen bond. We report now on the preparation of new hydridoacylphosphinorhodium(III) complexes, on their reactions with SPOs, and on the catalytic activity of these complexes to promote the release of hydrogen by hydrolysis of ammonia- or amine-boranes in air.

RESULTS AND DISCUSSION

Hydridoacylrhodium(III) Complexes. Hydridoacyl complexes [RhHCl(PPh₂(o-C₆H₄CO))L₂] (L = 4-pic, 1; iquin, 2) can be easily prepared by the reaction of [RhCl(COD)]₂ (COD = 1,5-cyclooctadiene) with PPh₂(o-C₆H₄CHO) (Rh/P = 1:1) in the presence of 4-methylpyridine (4-pic) or isoquinoline (iquin), with displacement of COD, as shown in

Scheme 1. This reaction is in line with the well-known ability of the aldehyde-phosphine ligand to promote the chelate-assisted

Scheme 1. Preparation of Hydridoacyl and $\{(Acylphoshine)(Diphenylphosphinous acid)\}$ Complexes $[RhHCl(PPh_2(o-C_6H_4CO))L_2]$ and $[RhHCl\{(PPh_2(o-C_6H_4CO))Ph_2L]^a$



^aReagents and conditions: (i) 25 °C in C_6H_6 . (ii) 40 °C in C_6H_6 . L = 4-pic (1) and (5); iquin (2) and (6); py (3) and (4).

oxidative addition of the aldehyde to late transition metal complexes.²⁹ Their ¹H and ³¹P{¹H} NMR spectra indicate the presence of only one species in solution. The ³¹P{¹H} NMR spectra contain only one doublet due to coupling with rhodium at 78 ppm, the characteristic low field due to the five-member ring effect.³⁰ The ¹H NMR spectra show a doublet of doublet in the high field region, due to a hydride bonded to rhodium (J(Rh,H) = 23 Hz) and *cis* to phosphorus (J(P,H) = 18 Hz), and the chemical shift, at -15.90 and -15.65 ppm for 1 and 2, respectively, is consistent with a hydride *trans* to chloride,³¹ although the geometry with hydride *trans* to nitrogen cannot be completely excluded. Complexes 1 and 2 are stable at room temperature in the solid state and decompose in solution within 1 day.

Complexes 1, 2, and also the previously reported [RhHCl- $(PPh_2(o-C_6H_4CO))(py)_2]$ (py = pyridine) $(3)^{32}$ react with diphenylphosphine oxide that displaces one N-donor ligand to afford complexes [RhHCl{(PPh₂(o-C₆H₄CO))(PPh₂O)H}L] (4-6) shown in Scheme 1. The ${}^{31}P{}^{1}H{}$ NMR spectra show two doublets of doublets at 98 and 62 ppm, due to the PPh₂OH ligand and to the chelating acyl-phosphine, respectively. The J(P,P) coupling constants, in the 410-414 Hz range, indicate two mutually trans phosphorus atoms (Figure S-1, Supporting Information). The ${}^{13}C{}^{1}H$ NMR spectra show the resonance due to the acyl group as a broad doublet (J(Rh,C) in the range 35-41 Hz) at the expected low field (248 ppm).³³ In the ¹H NMR spectra, the hydride appears as a doublet of triplets due to coupling to rhodium and to two cis phosphorus atoms with equal J(P,H). The hydride chemical shift, in the -14.40 to -14.51 ppm range, at slightly lower field than in complexes 1-2, may be due to the hydride being *trans* to nitrogen, although the possibility of the hydride being trans to chloride cannot be completely excluded. In the low field region, a sharp singlet at 11.8 ppm is also observed, which 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.^{2,34} Thus, complexes **4–6** contain a formally pincer PCP ligand in a meridional arrangement. As in irida- β -diketones,³⁵ a coplanar arrangement of the terdentate ligand appears to be a requirement for the formation of the hydrogen bond and leads to a *trans* disposition of the P atoms in complexes **4–6**, at variance with irida- β diketones requiring *cis* phosphorus atoms of the acyl-phosphine groups to afford the hydrogen bond.

The reaction of [RhHCl{(PPh₂(o-C₆H₄CO))(PPh₂O)H}-(py)] (4) with potentially chelating bidentate N-donors (LL) such as 2,2'-bipyridine (bipy), biacetyldihydrazone (bdh), biacetyloximehydrazone (boh), or 2-aminomethylpyridine (ampy) leads to displacement of pyridine and chloride to afford the cationic [RhH{(PPh₂(o-C₆H₄CO))(PPh₂O)H}-(LL)]⁺ complexes (7–10) (see Scheme 2) that were isolated as tetraphenylborate compounds, which behave as 1:1 electrolytes in acetone solution.

Scheme 2. LL = bipy (7); $H_2NN=C(CH_3)C(CH_3)=NNH_2$, bdh (8); $H_2NN=C(CH_3)C(CH_3)=NOH$, boh (9); 2- $(H_2NCH_2)C_5H_4N$, ampy (10)



As expected, the ${}^{31}P{}^{1}H$ NMR spectra of complexes 7 and 8 show the same pattern as 4, and their ${}^{13}C{}^{1}H$ NMR spectra show the resonances due to the acyl group at low field, 250 ppm. A doublet of doublet is observed for 7 due to coupling with rhodium (I(Rh,C) = 32 Hz) and with a *cis* phosphorus atom (J(P,C) = 4 Hz) and due to unobservable coupling to the second phosphorus atom (Figure S-2, Supporting Information). In the ¹H NMR spectra a doublet of triplets is observed at -12.96 or -12.71 ppm, respectively, which agree with hydride trans to nitrogen. At variance with the neutral complexes 4-6, in 7 the resonance due to the O-H---O moiety appears at 303 K as a broad signal at 12.16 ppm, which sharpens on lowering the temperature and becomes a sharp singlet (12.62 ppm) on reaching 223 K (Figure S-3, Supporting Information). The hydride and the ³¹P resonances remain unaltered upon lowering the temperature. For 8 two resonances are observed for the methyl groups of the bdh ligand, indicating nonequivalent imino fragments. Broad resonances are observed for O-H---O (12.34 ppm) and for the pendant amino groups (4.87 ppm) at 223 K. These results show that in 7 and 8 cleavage of the O-H---O hydrogen bond occurs readily in solution, thus allowing an equilibrium between species containing a terdentate ligand or a bidentate/monodentate pair of ligands (Scheme 2), with the former structure being stabilized at lower temperatures. A fast exchange of the bridging proton between the oxygen atoms has been assumed to occur in $[Rh(COD)\{(PR_2O)_2H\}]$ complexes.³⁴ In complex 8, containing a dihydrazone ligand, the pendant NH₂ groups can also be involved in this equilibrium. Hydroxyalkyl(bdh)rhodium(III) complexes have been shown to contain in the solid state an intramolecular O--- H–N bond involving the pendant NH₂ group.^{33a}

A X-ray diffraction study of 8 confirms the structure depicted in Scheme 2. Yellow single crystals of 8 for X-ray diffraction analysis were grown by slow diffusion of pentane into a THF solution. This compound crystallizes in the *Cc* space group and consists of mononuclear $[C_{35}H_{36}N_4O_2P_2Rh]^+$ cations, tetraphenylborate anions, and tetrahydrofuran as crystallization solvent. Figure 1 shows an ORTEP view of the molecular



Figure 1. ORTEP view of the cation in 8 (30% probability ellipsoids) showing the atomic numbering and the intramolecular hydrogen bond. All but two of the hydrogen atoms and the labels of some C atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh1–P1, 2.297(1); Rh1–P2, 2.322(1); Rh1–C1, 2.000(5); Rh1–N2, 2.123(4); Rh1–N3, 2.119(4); Rh1–H1, 1.418; C1–O1, 1.233(6); P2–O2, 1.595(3); O1–O2, 2.534(5); C1–Rh1–P1, 84.3(2); C1–Rh1–P2, 92.7(2); C1–Rh1–N2, 172.9(2); C1–Rh1–N3, 100.2(2); C1–Rh1–H1, 91.4; P2–Rh1–P1, 173.88(6); N3–Rh1–H1, 168.3; O1–H2–O2, 156.8(3).

structure of the cation and selected bond lengths and angles. The geometry about the metal atom is distorted octahedral, with the P atoms in the *trans* position. The equatorial plane is occupied by the imino N atoms of the dihydrazone ligand, the carbon atom of the acyl-phosphine, and the hydride. The Rh1–N2 and Rh1–N3 distances are equal and reflect a similar *trans* influence of acyl and hydride. The Rh1–P1 (2.297(1) Å) and the Rh1–P2 (2.322(1) Å) distances are slightly different, and this may be due to only P1 forming a five-membered chelation ring.^{33a}

This compound shows an intramolecular hydrogen bonding interaction, in which the O1 and O2 atoms are involved. The phosphinous acid proton could be clearly located as Fourier peaks in the difference map. The donor-acceptor O2---O1 distance (2.534(5) Å) is in accordance with moderately strong

hydrogen bonding between the phosphinous acid (O2-H2 0.851(3) Å) and the acyl group (O1---H2 1.729(4) Å). The O1-H2-O2 angle $(156.8(3)^\circ)$ is consistent with a O1---H2-O2 bridge. As expected for a hydrogen bonded phosphinous acid, the P2-O2 bond distance (1.595(3) Å) is between the values reported for single and double P-O bonds.^{1d,6e,34} The Rh1-C1 and the C1-O1 distances agree with those observed in other acylrhodium complexes.^{32,33a} The metallacycle comprising the acyl group and the phosphinous acid is essentially planar. The maximum deviation from the mean plane formed by the Rh1C1O1O2P2 atoms is 0.138 Å for C1. The metallacycle formed by the Rh1C1C2C7P1 atoms is also planar; the maximum deviation atom from the mean plane is 0.091 Å for C1. These metallacycles form a dihedral angle of 12.46°. As expected, the metallacycle Rh1C1C2C7P1 and the phenyl ring C2C3C4C5C6C7 are practically coplanar and form a dihedral angle of 6.07°. The THF molecule is bonded to the cationic unit by an intermolecular hydrogen bonding interaction, via H1N, between the pendant N1 of the diacetydihydrazone ligand and the O3 atom of the solvent (O3-N1, 2.922(5) Å; O3-H1N-N1, 167.9(3)°).

Complexes 9 and 10, containing nonsymmetric ligands, show fluxional behavior in solution. We performed a variable temperature NMR study on a CDCl₃ solution of 9 in the 223-323 K range. The low solubility of 10 precluded a similar study. At 223 K the ³¹P{¹H} NMR spectrum of 9 contains two sets of signals and the ¹H NMR spectrum contains also two sets of resonances due to the coordinated boh ligand, indicating the presence of two isomers 9a and 9b (Scheme 3), which differ in

Scheme 3. Exchange between 9a and 9b, Fast at Room Temperature and Slow at Low Temperature



the group trans to the hydride, oxime or hydrazone. On raising the temperature, the signals due to 9a and 9b broaden, coalescence occurs at 273 K, and the appearance of only one set of resonances, sharp at 313 K, occurs. At 223 K the hydride appears as a multiplet, which remains unaltered in the whole temperature range (Figure S-4, Supporting Information). No resonance is observed for the phosphinous acid proton. From line-shape analysis³⁶ of the variable temperature ³¹P{¹H} NMR spectra of complex 9 (Figure 2), a global value of $\Delta G^{\ddagger} = 52 \pm 1$ kJ mol⁻¹ has been determined using the Eyring equation.³⁷ The signals of the isomers are extremely close, and the experimental values of the rate constant k as a function of T are not accurate enough to determine ΔH^{\ddagger} and ΔS^{\ddagger} . Most likely, chelateopening, whether diimine or acyl-phosphine, can account for the observed fluxional behavior. Opening of acyl-phosphine chelate has been found to be responsible for a related exchange in diacylrhodium(III) complexes.³²

Catalytic Activity in the Hydrolytic Release of Hydrogen from Ammonia- or Amine-Borane Adducts. Complexes 1-10 were tried as catalysts for the hydrolysis of ammonia- or amine-borane adducts in THF/H₂O mixtures under mild temperatures, in the presence of air. According to eq 1, up to three equivalents of hydrogen per equivalent of adduct may be released.

$$RR'HN-BH_3 + 4H_2O$$

$$\rightarrow RR'NH_2^+ + B(OH)_3 + OH^- + 3H_2$$
(1)

A THF/H₂O = 9:1 ratio was required when using complexes 1-3 as catalysts due to their low solubility while for complexes 4-10 a THF/H₂O = 1:1 ratio was found optimal to attain the maximum hydrogen release rate. Performing these reactions with higher amounts of water led to precipitation of the catalyst. In the presence of Hg, similar results were obtained, confirming the homogeneous nature of the catalytic reaction.^{22c} Figure 3 shows the hydrogen release from AB (40 °C) in the presence of the representative complexes 1, 5, 7, 9, and 10 and a blank test in the absence of catalyst. The reaction rates and the conversion depend markedly on the catalyst. Significant differences in reaction rates were found; neutral complexes 1 and 5, containing monodentate N-donor ligands, are efficient homogeneous catalysts for this reaction while cationic complexes 7-10, containing chelating ligands, show a much lower activity. The blank test under the same experimental conditions, but in the absence of catalyst, shows that the hydrolysis of AB affords up to 9% of the maximum hydrogen content after 3.5 min.

Because of their higher efficiency, the catalysts 1 and 5 were chosen to perform kinetic studies. The kinetic profiles obtained with 1 do not show a defined kinetic model, and only the runs obtained with 5 were considered in this part of the study. Figure 4 shows the kinetic profiles for the hydrolysis of AB, tertbutylamine-borane (TBAB), and dimethylamine-borane (DMAB) with 5 as catalyst at 40 °C. A blank test under the same experimental conditions, but in the absence of 5, shows that the hydrolysis of TBAB or DMAB affords up to 13% or 12% of the maximum hydrogen content, respectively, and similar profiles to AB. After completion of the catalytic reactions, the ¹¹B 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.^{22a,b} By following the course of the catalytic hydrolysis of AB by NMR in THF- d_8 -D₂O mixtures, the evolution of hydrogen and the concomitant disappearance of AB with formation of borate were observed (Figures S-5 and S-6, Supporting Information). Neither borane nor metal-containing intermediates could be observed. As already observed for hydridoirida- β -diketones,²³ complex 5 shows very low activity to hydrolyze the triethylamine-borane adduct, which lacks a NH functionality.

Paying attention to the experimental data along runs, it can be said that there is not a simple kinetic model that can explain properly the behavior of the different chemical systems. Obviously, the observed data include the evolution of H_2 from both the uncatalyzed and the catalyzed reactions; the uncatalyzed reaction is always significant during the first stages of reaction, but afterward it reaches equilibrium (Figure 3), as confirmed by ¹H NMR (Figure S-7, Supporting Information). On the other hand, the catalyzed reactions practically take the hydrogen evolution to completion; in fact more than 2.5 equiv of hydrogen was always obtained, regardless the substrate used, and the final value is closer to 3.0 as temperature gets higher. The global process is the sum of both the uncatalyzed and catalyzed reactions. We have tried several kinetic approaches to obtain a suitable integrated rate law, but all of them have been



Figure 2. Variable-temperature ${}^{31}P{}^{1}H$ NMR spectra of 9 in CDCl₃: (left) experimental; (right) calculated. Calculated NMR spectra were obtained using the simulation program gNMR version 5.0.³⁶



Figure 3. Hydrogen release from AB in THF/H₂O mixtures using an initial substrate concentration of 0.46 M and a 0.5 mol % of 1 (\Box), 5 (\bullet), 7 (\bigcirc), 9 (\triangle), or 10 (\diamond) as catalyst; (\times) corresponds to a blank test (no catalyst present). *T*, 40 °C.

unsuccessful. However, a first-order approach can be applied with reasonably good results in every case: AB, TBAB, and DMAB. The overall rate constant, k_{obs} , can, then, be determined with comparison purposes. Under first-order conditions, the hydrogen concentration generated, at any time, can be given by eq 2:



Figure 4. Hydrogen release from AB (\Box), TBAB (\bigcirc), or DMAB (\triangle) as substrates, with initial substrate concentration of 0.46 M, in the presence of 0.5 mol % of **5** as catalyst in THF/H₂O mixtures. *T*, 40 °C. Open marks represent the experimental points. Solid lines represent the simulated behavior.

$$[H_2]_t = 3[substrate]_0(1 - e^{-k_{obs}t})$$
⁽²⁾

where the subscripts t and 0 represent time t and zero, respectively. The value of the hydrogen concentration evolved at completion, $[H_2]_{\infty}$ (= 3[substrate]₀), was experimentally obtained for every run from % conversion (Table 1). Using the

Table 1. % Conversion, Time Required, and Rate Constants for the Hydrolysis of Ammonia- and Amine-Boranes with $[RhHCl{(PPh_2(o-C_6H_4CO))(PPh_2O)H}(4-pic)]$ (5) (0.5 mol %) and THF/H₂O = 1:1 ratio

Substrate	$T/^{\circ}C$	% Conversion	Time/s	$10^3 k_{\rm obs} / {\rm s}^{-1}$
AB	25	89.5	3000	1.54 ± 0.07
	30	91.2	2400	2.6 ± 0.1
	35	96.6	1200	3.63 ± 0.08
	40	98.9	750	5.2 ± 0.1
	45	100	450	7.5 ± 0.2
TBAB	25	88.9	2700	0.95 ± 0.05
	30	86.9	1800	1.08 ± 0.05
	35	91.4	900	1.64 ± 0.05
	40	99.2	540	3.3 ± 0.1
	45	100	300	4.6 ± 0.2
DMAB	25	88.4	3600	0.44 ± 0.04
	30	93.9	2400	1.04 ± 0.07
	35	95.0	1800	1.8 ± 0.2
	40	100	900	1.65 ± 0.06
	45	100	540	3.2 ± 0.1

values of $[H_2]_{\infty}$, the experimental points corresponding to three half-times (88% completion) were fitted to eq 2 by nonlinear least-squares regression to obtain the value of the rate constant, k_{obs} . The value of k_{obs} together with the experimental value of the hydrogen equivalents released at equilibrium (Table 1) can be used to simulate the kinetic profiles and to evaluate the agreement of the kinetic model with the experimental data (Figure 4). The agreement of the experimental data to eq 2 indicates that the reaction rate can be considered first order with respect to [substrate]. Consequently k_{obs} shows no dependence on [substrate]₀, as experimentally confirmed.

The rate of hydrogen release depends also on the catalyst loading. The reaction rate, v_{exp} , collects the uncatalyzed, v_{uncat} , and the catalyzed v_{cat} reaction rates. If we assume a first-order dependence with respect to [catalyst]₀, the rate law agrees with

$$v_{\text{exp}} = (k_{\text{uncat}} + k_{\text{cat}} [\text{catalyst}]_0) [\text{substrate}]$$
(3)

where

$$k_{\text{uncat}} + k_{\text{cat}}[\text{catalyst}]_0) = k_{\text{obs}} \tag{4}$$

Figure 5 shows a plot of k_{obs} versus $[catalyst]_0$ for catalyst concentrations in the 1.13×10^{-3} to 4.6×10^{-3} M range, from which a first-order dependence on $[catalyst]_0$ can be proposed. The slope and the intercept of the plot in Figure 5 afford values for $k_{cat} = 1.26 \pm 0.12$ M⁻¹ s⁻¹ and $k_{uncat} = (1.6 \pm 0.3) \times 10^{-3}$ s⁻¹, respectively.

The temperature has a definitive influence on the conversion extent, which reaches 100% when $T \ge 40$ °C, regardless of what the substrate may be (Table 1). As shown in Figure 4, at 40 °C complex 5 requires 12.5, 9, or 15 min for complete hydrogen release from AB, TBAB, or DMAB, respectively. The hydrolysis of AB is similar to that observed when using hydridoirida- β -diketones.^{23b} Inspection of Figure 4 suggests some kind of deactivation in the AB hydrolysis when reaching 60% of reaction aproximately. On the other hand, the catalyst



Figure 5. Influence of $[\text{catalyst}]_0$ on k_{obs} for the hydrogen release from AB with **5** as catalyst in THF/H₂O mixtures. Standard deviations of slope and intercept are given in parentheses.

keeps its efficiency after completion. The kinetic profiles of the AB hydrolysis are practically reproduced once and again when the leftover solution of a completed reaction is used as the solvent for the next (Figure 6). We believe that the formation



Figure 6. Consecutive runs of hydrogen release from AB using 0.5 mol % of 5 as catalyst in THF/H₂O mixtures. *T*, 40 °C. Open marks represent experimental points; solid lines represent the simulated behavior.

of some less active form of the substrate, more easily formed by AB than by TBAB, and not the catalyst, is responsible for conversions under 100% at lower temperatures and for longer reaction times for AB than for TBAB.

The values of k_{obs} , obtained at several temperatures, will correspond to an average of three successive overlapped reactions in hydrogen generation. In such cases the rate constant usually lowers for the successive reactions and the value of k_{obs} will be a composite including the uncatalyzed reaction.

CONCLUSIONS

This report has shown that the reaction of hydridoacylrhodium-(III) complexes with diphenylphosphinous acid allows the preparation of new neutral and cationic derivatives containing a moderately strong O---H---O hydrogen bond between the acyl and the diphenylphosphinous acid fragments, thus leading to a formally pincer PCP ligand in a meridional arrangement. Neutral complexes are efficient homogeneous catalysts for the hydrolysis of ammonia- or amine-borane adducts in air to produce hydrogen. Kinetic studies indicate a complex kinetic model. A first-order approach on substrate and catalyst concentrations can be applied with reasonably good results for the neutral catalyst containing diphenylphosphinous acid. The catalyst can be reused at least for six runs, reproducing the kinetic profiles.

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)]₂,³⁸ [RhClH(PPh₂(o-C₆H₄CO))-(py)₂] (3),³² and PPh₂(o-C₆H₄CHO)³⁹ 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, and ¹H and ¹³C{¹H} (TMS internal standard) and ³¹P{¹H} (H₃PO₄ external standard) were measured from CDCl₃ solutions.

Preparation of [RhClH(PPh₂(o-C₆H₄CO))L₂] (L = 4-methylpyridine, 1; isoquinoline, 2). 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 PPh₂(o-C₆H₄CHO) (0.12 mmol) and stirring at room temperature for 2 h gave a yellow solid that was filtered off, washed with benzene, and dried under vacuum. Data for 1. Yield: 59%. IR (KBr, cm^{-1}): 2009 (m), ν (Rh–H); 1626(s), ν (C=O). ¹H NMR: (CDCl₃): δ – 15.90 (dd, 1H, I(Rh,H) = 22.9 Hz, I(P,H) = 18.0 Hz, RhH); 2.16 (s, 3H, CH₃); 2.34 (s, 3H, CH₃). ³¹P{¹H} NMR (CDCl₃): δ 77.8 (d, J(Rh,P) = 165 Hz). Anal. Calcd for $C_{31}H_{29}ClN_2OPRh$; C 60.55, H 4.75, N 4.56; found C 60.59, H 5.15, N 4.44. Data for 2. Yield: 62%. IR (KBr, cm⁻¹): 2050 (m), ν (Rh–H); 1630 (s), ν (C=O). ¹H NMR: $(\text{CDCl}_3): \delta - 15.65 \text{ (dd, 1H, } J(\text{Rh,H}) = 22.9 \text{ Hz}, J(\text{P,H}) = 17.9 \text{ Hz},$ RhH). ${}^{31}P{}^{1}H$ NMR (CDCl₃): δ 78.4 (d, J(Rh,P) = 165 Hz). Anal. Calcd for C37H29ClN2OPRh.C6H6; C 67.51, H 4.61, N 3.66; found C 67.76, H 4.75, N 3.70.

Preparation of [RhHCl{(PPh₂(o-C₆H₄CO))(PPh₂O)H]L] (L = pyridine, 4; 4-methylpyridine, 5; isoquinoline, 6). To a benzene suspension of [RhClH(PPh₂(o-C₆H₄CO))(L)₂] (0.06 mmol) was added diphenylphosphine oxide (0.06 mmol). Stirring for 24 h at room temperature or 6 h at 40 °C afforded a yellow solution. Addition of hexane gave yellow precipitates, which were filtered off, washed with hexane, and dried under vacuum. Data for 4. Yield: 83%. IR (KBr, cm⁻¹): 2048 (m), ν (Rh–H); 1644(m), ν (C=O). ¹H NMR (CDCl₃): δ -14.51 (dt, 1H, J(Rh,H) = 20.0 Hz, J(P,H) = 9.4 Hz, RhH); 11.77 (s, 1H, Ph₂P(O)H). ${}^{31}P{}^{1}H$ NMR (CDCl₃): δ 98.2 (dd, J(P,P) = 411 Hz, $J(Rh,\tilde{P}) = 129$ Hz, $Ph_2P(O)H$; 62.1 (dd, J(Rh,P) = 121 Hz, $PPh_2(o-C_6H_4CO)$). ¹³C{¹H} NMR (CDCl₃): δ 247.9 (d, J(Rh,C) = 35 Hz, C=O). Anal. Calcd for C₃₆H₃₁ClNO₂P₂Rh; C 60.90, H 4.40, N 1.97; found C 60.65, H 4.25, N 2.29. Data for 5. Yield: 60%. IR (KBr, cm⁻¹): 2051 (m), ν (Rh–H); 1620(m), ν (C=O). ¹H NMR $(CDCl_3): \delta -14.50 \text{ (dt, 1H, } J(Rh,H) = 19.8 \text{ Hz, } J(P,H) = 9.4 \text{ Hz},$ RhH); 2.04 (s, 3H, CH₃); 11.81 (s, 1H, Ph₂P(O)H). ${}^{31}P{}^{1}H{}$ NMR $(CDCl_3): \delta$ 98.2 (dd, J(P,P) = 414 Hz, J(Rh,P) = 128 Hz, $Ph_2P(O)H$; 61.9 (dd, J(Rh,P) = 121 Hz, $PPh_2(o-C_6H_4CO)$). ¹³C{¹H} NMR (CDCl₃): δ 248.2 (d, J(Rh,C) = 41 Hz, C=O); 29.8 (s, CH₃). Anal. Calcd for C₃₇H₃₃ClNO₂P₂Rh; C 61.38, H 4.59, N 1.93; found C 61.00, H 4.53, N 1.97. Data for 6. Yield: 63%. IR (KBr, cm⁻¹): 2048 (m), ν (Rh–H); 1632(m), ν (C=O). ¹H NMR (CDCl₂): δ -14.50 (dt, 1H, J(Rh,H) = 19.8 Hz, J(P,H) = 9.4 Hz, RhH); 11.86 (s, 1H, Ph₂P(O)H]). ³¹P{¹H} NMR (CDCl₃): δ 98.7 (dd, J(P,P) = 410 Hz, J(Rh,P) = 129 Hz, $Ph_2P(O)H)$; 62.2 (dd, J(Rh,P) = 121 Hz, $PPh_2(o-C_6H_4CO)$). ¹³C{¹H} NMR (CDCl₃): δ 248.2 (d, J(Rh,C) = 39 Hz, C=O). Anal. Calcd for C₄₀H₃₃ClNO₂P₂Rh; C 63.21, H 4.38, N 1.84; found C 63.57, H 4.78, N 2.29.

Preparation of $[RhH{(PPh_2(o-C_6H_4CO))(PPh_2O)H}(LL)]BPh_4$ (LL = 2,2'-bipyridine, 7; biacetyldihydrazone, 8; biacetyloximehydrazone, 9; 2-(aminomethyl)pyridine, 10). To a methanol suspension of 4 (0.06 mmol) was added 0.06 mmol of the corresponding ligand. Stirring for 1 h at room temperature afforded a yellow solution. Addition of NaBPh₄ (0.06 mmol) gave yellow solids that were filtered off, washed with methanol, and dried under vacuum. Data for 7. Yield: 51%. IR (KBr, cm⁻¹): 2040 (m), ν (Rh-H); 1599(m), ν (C=O). ¹H NMR (CDCl₃, 303 K): δ -12.96 (dt, 1H, J(Rh,H) = 21.0 Hz, J(P,H) = 10.4 Hz, RhH); 12.16 (s, br, 1H, Ph₂P(O)H). ³¹P{¹H} NMR (CDCl₃, 303 K): δ 105.1 (dd, J(P,P) =359 Hz, J(Rh,P) = 121 Hz, Ph₂P(O)H); 61.7 (dd, J(Rh,P) = 113 Hz, $PPh_2(o-C_6H_4CO))$. ¹³C{¹H} NMR (CDCl₃, 303 K): δ 250.4 (dd, J(Rh,C) = 32 Hz, J(P,C) = 4 Hz, C=O). Λ_{M} (ohm⁻¹cm² mol⁻¹): 80 (acetone). Anal. Calcd for C₆₅H₅₄BN₂O₂P₂Rh; C 72.91, H 5.08, N 2.62; found C 73.05, H 5.22, N 2.92. Data for 8. Yield: 55%. IR (KBr, cm⁻¹): 3401(m), 3309(m), ν (N–H); 2047 (m), ν (Rh–H); 1578 (m), ν (C=O). ¹H NMR (CDCl₃, 223 K): δ -12.89 (dt, 1H, J(Rh,H) = 20.8 Hz, J(P,H) = 10.1 Hz, RhH); 0.86 (s, 3H, CH₃), 0.81 (s, 3H, CH₃); 4.87 (br, 4H, NH₂); 12.34 (br, 1H, Ph₂P(O)H]). ³¹P{¹H} NMR (CDCl₃, 223 K): δ 104.3 (dd, J(P,P) = 337 Hz, J(Rh,P) = 119Hz, $Ph_2P(O)H$; 63.1 (dd, J(Rh,P) = 112 Hz, $PPh_2(o-C_6H_4CO)$). ¹³C{¹H} NMR (CDCl₃, 303 K): δ 251.5 (d, *J*(Rh,C) = 28 Hz, C=O); 13.1 (s, CH₃); 12.4 (s, CH₃). $\Lambda_{\rm M}$ (ohm⁻¹cm² mol⁻¹): 73 (acetone). Anal. Calcd for C59H56BN4O2P2Rh; C 68.88, H 5.49, N 5.45; found C 68.67, H 5.52, N 5.45. Data for 9. Yield: 68%. IR (KBr, cm⁻¹): 3388(m), 3300(w), ν (N–H); 2032 (m), ν (Rh–H); 1599 (m), ν (C= O). $\Lambda_{\rm M}$ (ohm⁻¹cm² mol⁻¹): 82 (acetone). Anal. Calcd for C50H55BN2O2P2Rh; C 68.81, H 5.38, N 4.08; found C 68.84, H 5.79, N 4.04. ¹H NMR (CDCl₃, 223 K): δ –12.22 (m, 2H, RhH); 0.82 (s, 3H, CH₃); 0.86 (s, 3H, CH₃); 0.93 (s, 3H, CH₃); 0.97 (s, 3H, CH₃); 4.78 (s, 2H, NH₂); 5.16 (s, 2H, NH₂). ¹³C{¹H} NMR (CDCl₃, 303 K): δ 246.2 (d, J(Rh,C) = 31 Hz, C=O). Data for 9a. ³¹P{¹H} NMR (CDCl₃, 223 K): δ 108.3 (dd, J(P,P) = 344 Hz, J(Rh,P) = 132Hz, $Ph_2P(O)H$; 57.6 (dd, J(Rh,P) = 114 Hz, $PPh_2(o-C_6H_4CO)$). Data for 9b. ${}^{31}P{}^{1}H$ NMR (CDCl₃, 223 K): δ 105.7 (dd, J(P,P) =339 Hz, J(Rh,P) = 130 Hz, $Ph_2P(O)H$; 55.0 (dd, J(Rh,P)= 115 Hz, PPh₂(o-C₆H₄CO)). Data for 10. Yield: 48%. IR (KBr, cm⁻¹): 3425 (sh), ν (N–H); 2033 (m), ν (Rh–H); 1616(m), ν (C=O). ¹H NMR $(CDCl_3, 303 \text{ K}): \delta - 13.81 \text{ (m, 1H, Rh}H); 3.49 \text{ (s, 2H, CH}_2); 3.81 \text{ (br,}$ 2H, NH₂). ³¹P{¹H} NMR (CDCl₃): δ 98.0 (dd, J(P,P) = 385 Hz, J(Rh,P) = 132 Hz, $Ph_2P(O)H$; 55.9 (dd, J(Rh,P) = 112 Hz, $PPh_2(o C_6H_4CO$)). Λ_M (ohm⁻¹cm² mol⁻¹): 85 (acetone). Anal. Calcd for C₆₁H₅₄BN₂O₂P₂Rh; C 71.64, H 5.32, N 2.74; found C 71.21, H 5.13, N 2.99.

X-ray Structure Determination of 8. A suitable crystal of 8 was mounted on a glass fiber and used for data collection on a Bruker AXS APEX CCD area detector equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) by applying the ω -scan method. Lorentz-polarization and empirical absorption corrections were applied. The structure was solved by direct methods and refined with full-matrix least-squares calculations on F^2 using the program SHELXS97.40 Anisotropic temperature factors were assigned to all atoms except for hydrogen atoms. The hydrogen atoms were included in the calculated position and refined riding on their respective carbon atoms with the thermal parameter related to the bonded atoms, with two exceptions. The hydride atom H1, located 1.418 Å from the metallic center, and the H2 atom of the phosphinous acid, involved in intramolecular hydrogen interaction, have been found in a difference Fourier and included and refined riding on the Ir or O atoms. Details on the data collection and analysis can be found in Table S-1, Supporting Information.

Dehydrogenation of RR'R"N–BH₃ with Complexes 1–10. A typical dehydrogenation experiment is described here for the hydrolysis of H_3N-BH_3 using 2.70 mL of THF/H₂O = 9:1 (1–3) or 1:1 (4–10) 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 buret. The solution was warmed to the required temperature and allowed to equilibrate for at least 10 min. A warmed solution of 0.006 mmol of the corresponding catalyst in dry THF was then syringed through the septum, and 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 buret. Volumes were measured at atmospheric pressure in the 25-45 °C range.

ASSOCIATED CONTENT

Supporting Information

NMR spectra of complexes **4**, **7**, and **9** and of the catalyzed and uncatalyzed hydrolysis of AB; and crystallographic data file of complex **8** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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