

Imine Hydrolysis and Role of a Rhodium(I)–Imine–Amine Complex in Homogeneous H₂-Hydrogenation of the Imine and a Rare Example of Inequivalent NH₂ Protons

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A Rh-catalyzed, homogeneous hydrogenation of the imine, PhCH₂N=CHPh, is shown to involve a Rh–imine–amine species that subsequently activates H₂, the amine (benzylamine) being formed via a Rh-catalyzed hydrolysis of the imine by adventitious water. The imine–amine complex, *cis*-{Rh[P(*p*-tolyl)₃]₂(PhCH₂N=CHPh)(NH₂CH₂Ph)}-PF₆ (**2b**), is structurally characterized, and the solution ¹H NMR data reveal inequivalent NH₂ protons.

Introduction

Mechanisms of catalytic, homogeneous H₂-hydrogenation of imines are poorly understood, relative to those of corresponding reductions of C=C and C=O functionalities, partly because the more forcing conditions that are required complicate experimental investigations and, further, the amine product can poison the catalyst.^{1,2}

During studies with the catalyst precursor [Rh(COD)-(PPh₃)₂](PF₆) that homogeneously hydrogenates aldimines under mild conditions,^{3,4} we have discovered that an accompanying metal-promoted hydrolysis of the imine to amine (and aldehyde) plays a key mechanistic role in that a resulting mixed Rh(I)–imine–amine complex activates H₂ for subsequent hydrogenation of the imine. The findings are potentially significant regarding applications of imine hydrogenations.⁵

Experimental Section

General. Unless otherwise stated, synthetic procedures were performed at room temperature (rt, ~20 °C) using standard Schlenk techniques under an atmosphere of dry Ar. The liquid imine

PhCH₂N=CHPh and PhCH₂NH₂ were purchased from Aldrich and purified by distillation prior to use, while the solid imines PhCH₂N=C(Me)Ph and PhCH₂N=C(Ph)₂ were synthesized by Dr. D. Fogg⁶ of this laboratory. The [Rh(COD)(PR₃)₂](PF₆) and corresponding *cis*-[Rh(PR₃)₂(MeOH)₂](PF₆) precursors (R = Ph, *p*-tolyl) were prepared according to literature procedures.^{4,7,8} Other reagents were purchased from commercial sources and used as supplied. Solvents were dried over the appropriate agents and distilled under N₂ prior to use. NMR spectra were recorded on Bruker AV 300 (300 MHz for ¹H, 121 MHz for ³¹P{¹H}, 75 MHz for ¹³C) and AV 400 (400 MHz for ¹H, 162 MHz for ³¹P{¹H}, 100 MHz for ¹³C) spectrometers at 300 K. Residual solvent proton (¹H, relative to external SiMe₄ δ 0.00) and external P(OMe)₃ (³¹P{¹H}, δ 141.00 vs external 85% aq H₃PO₄) were used as references. All *J* values are given in hertz. Infrared spectra were recorded on an ATLI Mattson Genesis Series FTIR spectrophotometer (range 500–4000 cm⁻¹), and all IR (KBr pellet) bands are reported in cm⁻¹. GC analyses were performed on a Hewlett-Packard 5890A instrument equipped with an HP 17 capillary column (He carrier gas) and an FID detector. Elemental analyses were performed by Mr. P. Borda of this department using a Carlo Erba 1108 analyzer.

Syntheses. *cis*-[Rh(PR₃)₂(PhCH₂N=CHPh)(PhCH₂NH₂)](PF₆) (**R** = Ph, **2a**; *p*-Tolyl, **2b**). A red solution of *cis*-[Rh(PR₃)₂(MeOH)₂](PF₆) (0.08 mmol) in MeOH (3 mL) was treated with excess PhCH₂N=CHPh (57.0 μL, 0.304 mmol) under Ar, and the mixture stirred at rt for 24 h; spontaneous precipitation of a light-orange solid occurred. This was collected, washed with Et₂O (3 × 4 mL), and dried in vacuo.

R = Ph (**2a**). Yield: 0.044 g (45%). Anal. Calcd for C₅₇H₅₂N₂P₃F₆Rh: C, 63.70; H, 4.88; N, 2.61. Found: C, 63.67; H,

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Table 1. Crystallographic Data for **2b**

2b	
formula	C ₆₃ H ₆₄ F ₆ N ₂ P ₃ Rh
fw	1158.98
cryst color, habit	orange, plate
cryst size (mm ³)	0.52 × 0.32 × 0.12
space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	11.5104(14)
<i>b</i> (Å)	19.986(2)
<i>c</i> (Å)	25.219(4)
β (deg)	99.299(9)
<i>V</i> (Å ³)	5725.3(13)
μ (mm ⁻¹)	0.442
total reflns	41237
unique reflns	10051
<i>R</i> _{int}	0.0482
no. variables	683
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>))	0.0415 (7604 obsd reflns)
w <i>R</i> 2 ^a	0.1096 (all data)
GOF	1.016 (all data)

$$^a w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 7.755P], \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

4.69; N, 2.63. ¹H NMR (300 MHz, CD₂Cl₂): δ 1.13 (t, 1H, NH₂, ²*J*_{HH} = 12), 1.29 (t, 1H, NH₂, ²*J*_{HH} = 12), 2.52 (2 td, 2 H, CH₂, ²*J*_{HH} = 13, ³*J*_{HH} = 3), 2.63 (2 td, 2H, CH₂, ²*J*_{HH} = 13, ³*J*_{HH} = 3), 4.40 (d, 1H, CH₂, ²*J*_{HH} = 13), 5.12 (d, 1H, CH₂, ²*J*_{HH} = 13), 5.98 (d, 2H, *o*-C₆H₅, ³*J*_{HH} = 7), 6.95–7.90 (m, 41H, Ar), 8.01 (bs, 1H, N=CH), 9.70 (d, 2H, *o*-C₆H₅, ³*J*_{HH} = 7). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ 46.94 (dd, *J*_{RhP} = 166, ²*J*_{PP} = 49), 50.07 (dd, *J*_{RhP} = 180, ²*J*_{PP} = 49). IR (KBr pellet): ν = 1616 (C=N), 3313 (N–H).

R = *p*-Tolyl (2b). Yield: 0.047 g (50%). Anal. Calcd for C₆₃H₆₄N₂P₃F₆Rh: C, 65.29; H, 5.57; N, 2.42. Found: C, 65.26; H, 5.61; N, 2.43. ¹H NMR (300 MHz, CD₂Cl₂): δ 1.13 (t, 1H, NH₂, ²*J*_{HH} = 12), 1.23 (t, 1H, NH₂, ²*J*_{HH} = 12), 2.31 (s, 9H, *p*-CH₃), 2.33 (s, 9H, *p*-CH₃), 2.50 (td, 1H, CH₂, ²*J*_{HH} = 13, ³*J*_{HH} = 3), 2.58 (td, 1H, CH₂, ²*J*_{HH} = 13, ³*J*_{HH} = 3), 4.38 (d, 1H, CH₂, ²*J*_{HH} = 12), 5.15 (d, 1H, CH₂, ²*J*_{HH} = 12), 5.95 (d, 2H, *o*-C₆H₅, ³*J*_{HH} = 7), 6.90–7.85 (m, 35H, Ar), 8.03 (bs, 1H, N=CH), 9.76 (d, 2H, *o*-C₆H₅, ³*J*_{HH} = 7). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ 45.15 (dd, *J*_{RhP} = 166, ²*J*_{PP} = 49), 48.20 (dd, *J*_{RhP} = 180, ²*J*_{PP} = 49). IR (KBr pellet): ν = 1601 (C=N), 3307 (N–H). An X-ray quality crystal of **2b** was obtained by slow evaporation at rt of a CD₃OD solution of the complex.

H₂-Hydrogenation Studies. These experiments were performed in a three-neck flask, with one neck connected to the H₂-inlet, a second neck fitted with a rubber septum that served as the sampling as well as the injection port for the imine, and the third neck used to charge the flask with solvent (MeOH, 10 mL) and catalyst precursor [Rh(COD)(PR₃)₂]PF₆ (up to 1.0 mM). After this mixture was reacted with H₂ (1 atm) at 30 °C for 1 h to form [Rh(H)₂(PR₃)₂(MeOH)₂]PF₆ (R = Ph, **1a**; *p*-tolyl, **1b**),^{4,7,8} excess imine (up to 100 mM) was injected via a microsyringe, and the stirred reaction mixture was sampled (5 μ L) periodically, with conversions being monitored by GC analysis. Systems were also monitored by H₂-absorption at 30 °C in a constant-pressure gas-uptake apparatus.⁹

X-ray Crystallographic Analysis. Measurements were made at 173(2) K on a Siemens SMART CCD diffractometer with graphite monochromated Mo K α radiation (0.71073 Å). Some crystallographic data for **2b** are shown in Table 1. The final unit-cell parameters were based on 354 reflections with 1.31° < θ < 24.99°. The structure was solved by direct methods and refined by full-matrix least-squares (SHELXL-97),¹⁰ using $w = 1/[\sigma^2(F_o^2) +$

(0.0478P)² + 7.755P], where $P = (F_o^2 + 2F_c^2)/3$. All non-H-atoms were refined anisotropically, and H-atoms were included in fixed positions.

Results and Discussion

The Imine–Amine Complex. The room temperature reaction of either *cis,trans,cis*-[Rh(H)₂(PR₃)₂(MeOH)₂]PF₆ (R = Ph, **1a**; *p*-tolyl, **1b**) or *cis*-[Rh(PR₃)₂(MeOH)₂]PF₆ (R = Ph or *p*-tolyl)^{4,7,8} with an excess of the liquid imine PhCH₂N=CHPh (either with imine/Rh = 4, as in the synthetic procedure, or with imine/Rh = 100, as used in catalytic conditions under 1 atm H₂, see below) in MeOH under Ar generates the Rh(I) complexes *cis*-[Rh(PR₃)₂(PhCH₂N=CHPh)(NH₂CH₂Ph)]PF₆ (R = Ph, **2a**; *p*-tolyl, **2b**), containing the η^1 -imine and η^1 -benzylamine, a hydrolysis product of the imine. In situ yields of **2a,b** are quantitative, while isolated yields are ~50%. Benzaldehyde, the coproduct of hydrolysis, was detected by GC and ¹H NMR analyses of the filtrate from the synthetic procedure; H₂ was also detected by ¹H NMR (δ 4.15). The hydrolysis is Rh-promoted, as the neat imines are stable in MeOH; we have noted elsewhere Ru-promoted¹¹ and Ir-promoted¹² hydrolytic cleavage of such imines.

The structure of **2b** (Figure 1a) reveals essentially square-planar geometry at Rh, while selected structural parameters are listed in Table 2; the C=N imine bond is some 0.2 Å shorter than the C–N bond of the amine. There is close contact between the phenyl *o*-H atoms of the amine and an imine Ph (e.g., C(53)⋯H(63) = 2.65 Å), which causes restricted rotation of these two moieties in the solid state structure and also in solution, see below. Furthermore, one of the *o*-protons of the imine Ph ring (H(49)) “docks” over, and is well within van der Waals distance (2.43 Å) with, the Rh; the implications of this close interaction are also evident in the solution structure, see below. The solid state IR spectrum shows $\nu_{C=N}$ and ν_{N-H} of the coordinated imine and amine, respectively.

The rt ³¹P{¹H} NMR spectrum of **2b** in CD₂Cl₂ shows the expected AMX, 8-line pattern due to inequivalence of the two phosphine ligands, and on the basis of *J*_{RhP} values,¹³ the upfield (δ 45.15 dd, *J*_{RhP} = 166, ²*J*_{PP} = 49) and downfield (δ 48.20 dd, *J*_{RhP} = 180, ²*J*_{PP} = 49) resonances are assigned to the P-atom *trans* to the imine and amine, respectively. The ¹H NMR data are unusual in that both the benzylic and NH₂ protons of the amine, and also the benzylic protons of the imine, are inequivalent. The amine benzylic protons appear as two triplets of doublets (δ 2.50 and 2.58, ²*J*_{HH} = 13, ³*J*_{HH} = 3), due to coupling to the NH₂ protons and to each other, and similarly the NH₂ resonances, although less well resolved, appear as two somewhat broadened triplets (δ 1.13 and 1.23, ²*J*_{HH} = 12). The NH₂ protons are inequivalent because of restricted rotation of the amine; similar behavior is seen in a Ru system involving again

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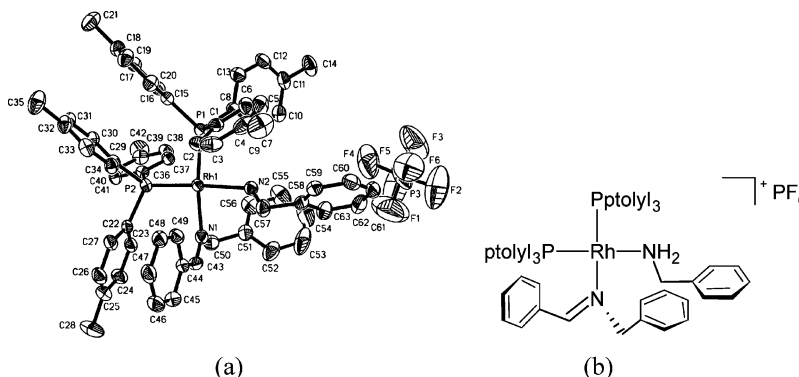


Figure 1. (a) ORTEP diagram of *cis*-[Rh[P(*p*-tolyl)₃]₂(PhCH₂N=CHPh)(NH₂CH₂Ph)]PF₆ (**2b**) with 50% probability thermal ellipsoids. (b) Schematic diagram of the imine-amine interactions within complex **2b**.

Table 2. Selected Bond Distances and Angles for *cis*-[Rh[P(*p*-tolyl)₃]₂(PhCH₂N=CHPh)(NH₂CH₂Ph)]PF₆ (**2b**) with Estimated Standard Deviations in Parentheses

bond	length (Å)	bond	angle (deg)
Rh(1)–P(1)	2.2538(12)	P(1)–Rh(1)–N(1)	172.46(10)
Rh(1)–P(2)	2.2503(12)	P(2)–Rh(1)–N(2)	176.16(10)
Rh(1)–N(1)	2.128(4)	P(1)–Rh(1)–P(2)	96.95(4)
Rh(1)–N(2)	2.209(3)	P(1)–Rh(1)–N(2)	86.41(10)
N(1)–C(50)	1.495(6)	P(2)–Rh(1)–N(1)	90.45(10)
N(1)–C(43)	1.288(6)	C(43)–N(1)–C(50)	116.1(4)
N(2)–C(57)	1.488(6)	C(50)–N(1)–Rh(1)	113.5(3)
C(43)–C(44)	1.459(7)	C(43)–N(1)–Rh(1)	130.3(3)
C(57)–C(58)	1.522(6)	C(57)–N(2)–Rh(1)	122.2(3)
C(50)–C(51)	1.507(7)	N(2)–C(57)–C(58)	111.8(4)

benzylamine that was also generated via Ru-promoted hydrolysis of PhCH₂N=CHPh.¹¹ The corresponding ¹H–¹H COSY NMR experiment shows strong correlation between the amine CH₂ and NH₂ signals, which are not affected by ³¹P-decoupling. The diastereotopically inequivalent benzylic protons of the imine are seen as two doublets at δ 4.38 and 5.15 (²J_{HH} = 12). The singlet resonance for the CH=N proton at δ 8.03 is upfield to that of the free imine (δ 8.50). Sharp doublets at δ 5.95 and 9.76 (³J_{HH} = 7), each integrating for two protons, are assigned to *o*-protons of phenyl rings, each coupling to a neighboring *m*-proton, because an rt ¹H–¹³C HETCOR NMR spectrum reveals correlation of these resonances with aromatic C-atoms. Consideration of the solid state structure (Figure 1a,b) suggests that these *o*-phenyl protons are those of the amine and imine, and not the phosphine, with the downfield resonance being attributed to the imine *o*-proton (H(49)) involved in a pseudoagostic interaction with the Rh. The rt NMR spectral data in CD₃OD, measured because the hydrogenation catalysis is carried out in MeOH, generally correspond closely to those in CD₂Cl₂, except that the NH₂ resonances are not seen because of H-exchange with the deuterated solvent, and thus, no coupling is seen to the NH₂ protons; the amine CH₂ protons appear as doublets instead of as a triplet of doublets. Also, the CH=N proton is now seen at δ 8.21, 0.2 ppm downfield of the value in CD₂Cl₂. The NMR data for **2a** in CD₂Cl₂ and in CD₃OD replicate those of **2b**, except for the absence of the Me proton resonances of the *p*-tolyl phosphines.

Catalytic Hydrogenation. In a typical catalytic hydrogenation experiment, PhCH₂N=CHPh undergoes complete reduction in ~30 min to dibenzylamine (Figure 2); an

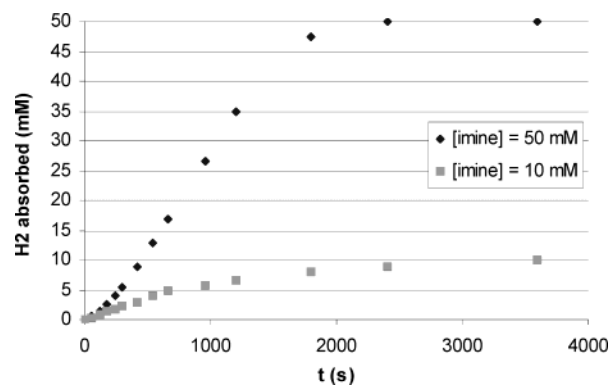


Figure 2. Plots of H₂ absorbed (mM) vs time for hydrogenation of PhCH₂N=CHPh (◆ = 50 mM; ■ = 10 mM) catalyzed by [Rh(COD)(PPh₃)₂]-PF₆ (0.50 mM) in MeOH under 1 atm H₂ at 30 °C.

induction period is observed during the first few minutes, followed by a linear region showing up to ~90% conversion, which corresponds to zero-order in [imine]. The linear rate for the upper curve is 3.5 × 10⁻⁵ M s⁻¹. The kinetics¹³ (see Figures S1–S3 in the Supporting Information) were determined from such maximum, linear rates, where the kinetic order in imine decreases from first-order at lower [imine] (<20 mM) to zero-order at higher [imine] (> 60 mM); indeed, at the lower [imine], the conversion plots gave (after the induction period) standard, logarithmic first-order plots for the imine dependence (Figure 2, lower curve). The linear rates are first-order in [Rh], and are first-order in [H₂] at both lower and higher [imine]. Addition of the dibenzylamine product does not inhibit the catalysis, but addition of benzylamine (the hydrolysis product) does decrease the hydrogenation rates, especially at lower [imine]. Of key importance, the only Rh species detected by NMR in the linear region of the conversion plots is **2a**, the imine-amine complex. Indeed, use of **2a** instead of **1a**, at the same [Rh], gives the same maximum rates, without any observed induction period. Similarly, there was no induction period when using an in situ **2a** catalyst made by addition of excess imine to a solution of the benzylamine complex *cis*-[Rh-(PPh₃)₂(NH₂CH₂Ph)(L)]PF₆ (Figure 3, L = MeOH, **3**; L = PhCH₂NH₂, **4**).¹⁴

These findings show unambiguously that the induction period is related to the imine hydrolysis and formation of **2a**. The proposed overall mechanism (Figure 3) shows the

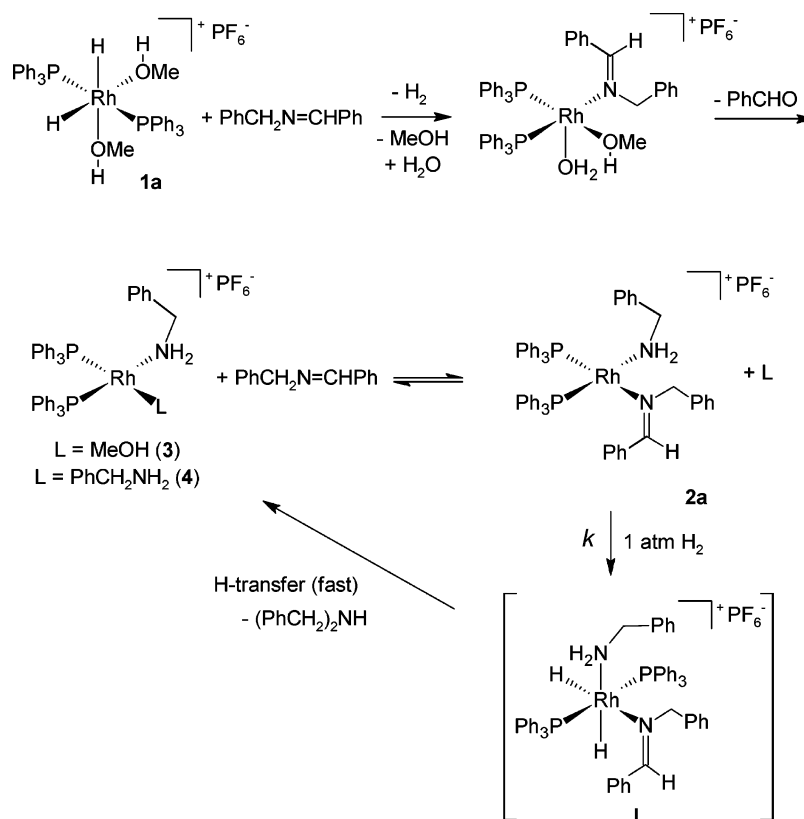


Figure 3. Suggested reaction steps for the hydrogenation of $\text{PhCH}_2\text{N}=\text{CHPh}$.

initial hydrolysis step that must involve loss of H_2 from **1a** and coordination of imine, but whether there is *trans*-attack by external $\text{H}_2\text{O}/\text{OH}^-$, or *cis*-attack by coordinated $\text{H}_2\text{O}/\text{OH}^-$, is unknown. Once the benzylamine–MeOH species **3** and the accompanying bis(amine) species **4**^{13,14} are formed, rapid pre-equilibria with imine give **2a**. A subsequent rate-determining (*k*) oxidative addition of H_2 gives a dihydrido–imine–amine species, and the catalytic cycle is completed by rapid hydrogen transfer with elimination of dibenzylamine product. This mechanism is consistent with the observed Michaelis–Menten type kinetics, the dependence on [imine] going from first-order at low [imine] to zero-order at higher [imine] when **2a** is fully formed; the mechanism also satisfies the first-order dependences on both [Rh] and $[\text{H}_2]$, and the limiting rate at 30 °C gives $k \sim 45 \text{ M}^{-1} \text{ s}^{-1}$. The noted inverse dependence on added L (PhCH_2NH_2) results from increased formation of the bis(benzylamine) species **4** (Figure 3, L = PhCH_2NH_2).¹⁴

The hydrolytic generation of 1 mol of benzylamine per Rh is clearly critical for the successful hydrogenation of $\text{PhCH}_2\text{N}=\text{CHPh}$. The addition of dibenzylamine (the hydrogenation product) does not inhibit the catalysis as this forms only a labile mono(dibenzylamine) species.²

Attempts to detect a dihydrido intermediate (**I**, Figure 3) by low temperature NMR were unsuccessful, and we can

offer no information on whether an η^2 -imine intermediate is necessary for hydrogenation; such a species, usually followed by stepwise transfer of two H-atoms via an alkylamido intermediate, has been invoked invariably in Rh-catalyzed,^{1,3,15} Ir-catalyzed,¹⁶ or Ti-catalyzed¹⁷ imine hydrogenations, although a shift to an η^2 -imine mode may be unnecessary.¹⁸ Concerted transfer of a coordinated hydride and a proton from an amine- NH_2 ¹⁹ could also be envisaged for our Rh system.

An “unsaturated” route, in which a rapidly formed Rh–imine complex reacts with H_2 in a slow step (cf. Figure 3), has been proposed earlier by our group (on the basis of NMR and minimal kinetic data) for high pressure imine hydrogenations catalyzed by $[\text{Rh}(\text{P}–\text{P})]^+$ systems, where P–P is a chelating diphosphine;^{1,15} whether a “prehydrolysis” step to generate a mixed imine–amine species was involved in these systems is unclear.

Liquid imines may be the source of H_2O , because of the lack of hydrolysis evident when using in synthetic procedures

(14) Species **3** and **4** are formed in situ from a 1:1 mixture of *cis*- $[\text{Rh}(\text{PPh}_3)_2(\text{CD}_3\text{OD})_2]\text{PF}_6$ and PhCH_2NH_2 in CD_3OD under Ar; **3**, like the corresponding dibenzylamine complex,² is fluxional at rt but is characterized below 283 K by δ_{P} 47.69 dd ($J_{\text{RHP}} = 169$) and 60.06 dd ($J_{\text{RHP}} = 214$) with $^2J_{\text{PP}} = 54$. The synthesis and structural characterization of **4**¹³ will be described elsewhere.

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(a) a $\text{PhCH}_2\text{N}=\text{CHPh}$ /Rh ratio of 1:1, or (b) the solid imines $\text{PhCH}_2\text{N}=\text{C}(\text{Ph})(\text{R})$ ($\text{R} = \text{Ph}$ or Me) at imine/Rh ratios of 2–100. Both systems a and b in MeOH generate the Rh(III)-hydrido-orthometalated complexes, $[\text{Rh}(\text{H})\{\text{PhCH}_2\text{N}=\text{C}(\text{R})(o\text{-C}_6\text{H}_4)\}(\text{MeOH})]\text{PF}_6$ ($\text{R} = \text{H}, \text{Ph}, \text{or Me}$),¹³ chemistry that will be described in detail elsewhere. Of note, neither of the solid imines was catalytically hydrogenated, even upon addition of H_2O ($\text{H}_2\text{O}/\text{imine} = 5$) to the system, while addition of benzylamine (amine/Rh = 1) to these systems also did not promote hydrogenation; again, in these attempted catalytic reactions, the Rh(III)-hydrido-orthometalated complexes noted above were generated. The orthometalated species ($\text{R} = \text{H}$) on treatment with water can be hydrolyzed (with loss of PhCHO) to the catalytically important amine–imine species, but whether the orthometalated species plays a direct role in the catalysis is unclear.²⁰

The chemistry of the corresponding Ir complexes is markedly different, presumably because of the stronger metal–hydride and metal–carbon bonds in the third row transition metal system.²¹ Thus, on treatment of *cis,trans,cis*- $[[\text{Ir}(\text{H})_2(\text{PPh}_3)_2(\text{MeOH})_2]\text{PF}_6$, the Ir analogue of **1a**, with excess $\text{PhCH}_2\text{N}=\text{CHPh}$ in MeOH under Ar, hydrolysis of 1 mol equiv of imine is again observed, but the product

generated is now the Ir(III) complex $[\text{Ir}(\text{H})(\text{PPh}_3)_2\{\text{PhCH}_2\text{N}=\text{CH}(o\text{-C}_6\text{H}_4)\}(\text{PhCH}_2\text{NH}_2)]\text{PF}_6$ containing the amine ligand and a chelated *N,C*-bound orthometalated imine;¹² this species does not catalyze hydrogenation of the imine under ambient conditions, and indeed, it reacts with H_2 to give the catalytically inactive, neutral, dihydrido complex $\text{Ir}(\text{H})_2(\text{PPh}_3)_2\{\text{PhCH}_2\text{N}=\text{CH}(o\text{-C}_6\text{H}_4)\}$.¹³

Conclusions

We have shown that an important feature of the Rh-catalyzed H_2 -hydrogenation of one imine ($\text{PhCH}_2\text{N}=\text{CHPh}$) in MeOH solution is hydrolysis of the imine and generation of a Rh–imine–amine species that subsequently activates H_2 to effect the catalysis. A key question remaining, and being studied, is whether such hydrolysis is important more generally to effect efficient imine hydrogenation.

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Supporting Information Available: X-ray crystallographic data for the structure of the **2b** in CIF format. Kinetic dependence on [imine] (Figure S1), [Rh] (Figure S2), and [H_2] (Figure S3) for hydrogenation of $\text{PhCH}_2\text{N}=\text{CHPh}$ in MeOH at 30 °C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(20) A reviewer suggested that a bis(imine) complex might be involved in generation of the benzylamine; this is certainly possible, but while Rh(I)–bis(imine) species are known,¹⁵ we have no evidence for such species within the $\text{PhCH}_2\text{N}=\text{CHPh}$ system.

(21) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 82, 286.