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Version Post-print/accepted manuscript

Citation Clapham, S. E.; Iuliis, M. Z.-D.; Mack, K.; Prokopchuk, D. E.;
(published version) Morris, R. H. *Can. J. Chem.* **2014**, 92, 731–738.

<http://doi.org/10.1139/cjc-2014-0060>

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This article is dedicated to Professor Barry Lever in recognition of his leadership role in inorganic chemistry in Canada.

Abstract

The hydrido-amido complex OsH(NHCMe₂CMe₂NH₂)(PPh₃)₂ (**1**) catalyzes the base-free hydrogenation of ketones in benzene. Kinetic studies using **1** revealed that the system has an induction period, after which the rate of the reaction increases. By adding a critical concentration of alcohol at the start of the reaction a constant rate was observed indicating that the reaction is autocatalytic in the product alcohol. Varying the initial conditions showed that the reaction rate is dependent on hydrogen and catalyst concentration and independent of ketone concentration. Above the critical concentrations of 1-phenylethanol, the reaction rate is independent of alcohol concentration. The rate law for pressures up to 5 atm was found to be: rate = d[Alcohol]/dt = -d[Ketone]/dt = k[Os][H₂], with k = 30 M⁻¹s⁻¹ at 293 K. Therefore the heterolytic splitting of dihydrogen is rate determining under these conditions. Surprisingly only small kinetic isotope effects were measured in contrast to the analogous ruthenium system. The thermodynamic values for the transition state of the rate limiting step were determined to be $\Delta H^\ddagger = 3.7$ kcal·mol⁻¹ and $\Delta S^\ddagger = -39$ cal·mol⁻¹ with a Gibbs free energy of activation of $\Delta G^\ddagger$ (293 K) = 15 kcal·mol⁻¹. Reactions of the amido-hydrido complex, OsH(NHCMe₂CMe₂NH₂)(PPh₃)₂, with the product alcohol, 1-phenylethanol, in benzene under Ar is partially converted into the dihydride complex, *trans*-OsH₂(NH₂CMe₂CMe₂NH₂)(PPh₃)₂ and acetophenone. As expected from these results, **1** is a ketone transfer hydrogenation catalyst in isopropanol. With excess alcohol, an osmium alkoxide is identified, at least in low temperature solutions.

Introduction

The mechanism of the homogenous H₂-hydrogenation under base-free conditions of ketones catalyzed by well-defined ruthenium complexes have been studied previously by our research group. These include *trans*-RuH₂(*R*-binap)(*t*men) where *t*men is NH₂CMe₂CMe₂NH₂,^{1; 2} RuH(NHCMe₂CMe₂NH₂)(PPh₃)₂,¹ (*S,S*)-RuHCl(PPh₂C₆H₄CH₂NHC₆H₁₀NHCH₂C₆H₄PPh₂)/KO*i*Pr³ and RuH(*app*)(*S*-binap), where *app* is the amide version of the ligand 2-amino-2-(2-pyridyl)-propane.⁴ An essential catalytic structure

contains a ruthenium-amido bond that causes the heterolytic splitting of H₂ producing a dihydride and an amine group on ruthenium. The diamine ligands tmen and app used in these studies do not possess β -hydrogen atoms in order to protect the amido form of the ligand from β -hydride elimination and the catalyst from decomposing. The concept of metal-ligand bifunctional catalysis, first proposed by Noyori, applies well to these catalytic systems.^{5;6} That is, both the metal and the ligand, in this case an amido group, participate in the heterolytic splitting of H₂, the rate-determining step of the reaction. Noyori's group studied the mechanism of hydrogenation of the benchmark substrate acetophenone in isopropanol using a well-defined precursor RuH(BH₄)(*S*-tolbinap)(*S,S*-dpen) and found that under basic conditions it also proceeded via rate-determining splitting of dihydrogen across the ruthenium-amido bond with a kinetic isotope effect (KIE) k_{H_2}/k_{D_2} of 2.0.⁷ We reported a k_{H_2}/k_{D_2} of 2.1 ± 0.1 for the hydrogenation of acetophenone in benzene catalysed by our *trans*-RuH₂(tmen)(*R*-binap) catalyst.² The use of KIE in the study of organometallic reaction mechanisms has recently been reviewed.⁸

In order to further explore the reactivity of the group 8 metal triad, the osmium (II) hydrido-amido complex OsH(HNCMe₂CMe₂NH₂)(PPh₃)₂ (**1**) and the *trans*-dihydride complex OsH₂(H₂NCCMe₂CMe₂NH₂)(PPh₃)₂ (**2**) were examined as catalysts in the hydrogenation of acetophenone to 1-phenylethanol in benzene. Initial experiments using **1** as a catalyst revealed an increase in the rate of reaction as the reaction proceeded.⁹ Such behaviour could indicate the operation of autocatalysis as first proposed for the system RuH(app)(*S*-binap);⁴ that is, the product alcohol speeds up the reaction by lowering the activation barrier for the rate determining step.

The autocatalytic behaviour of our RuH(app)(*S*-binap) system was attributed to the phenylethanol product assisting in the splitting of the H-H bond by inserting its -OH moiety into the four-membered ring of the Ru(H₂)(amido) transition state structure to produce a lower energy six-membered transition state, as shown in Figure 1, IV.⁴ Noyori and co-workers found that isopropanol was the best solvent for the H₂-hydrogenation of ketones. They had previously proposed a similar transition state structure.⁷ Alcohol-assisted transition states for other ruthenium based bifunctional H₂-hydrogenation catalysts were also suggested by Ikariya¹⁰ and Casey.¹¹

We describe here our investigation of the kinetics of catalysis by the OsH(NHCMe₂CMe₂NH₂)(PPh₃)₂ (**1**) complex.

materials was detected.

Reaction of OsH(NHCMe₂CMe₂NH₂)(PPh₃)₂ with 1-phenylethanol.

(a) Under argon, OsH(NHCMe₂CMe₂NH₂)(PPh₃)₂ (20 mg, 0.0230 mmol) and 1-phenylethanol (10 mg, 0.0819 mmol, ~ 3.6 eq.) were added to an NMR tube and dissolved in C₆D₆. An orange-red solution was observed. The ¹H and ³¹P{¹H} NMR spectra were obtained. The presence of **1** (¹H NMR(OsH) -24 ppm, br; ³¹P{¹H} NMR 29 ppm, br) and 1-phenylethanol were detected as well as the presence of *trans*-OsH₂(tmen)(PPh₃)₂ (**2**) (¹H NMR(OsH) -7.1 ppm; ³¹P{¹H} NMR 37 ppm) and acetophenone. Integration of the hydride peaks in the ¹H NMR spectrum of **1** and **2** provided a 1:1 hydride ratio, indicating a 2:1 ratio of **1** to **2**.

(b) Under argon, OsH(NHCMe₂CMe₂NH₂)(PPh₃)₂ (9 mg, 0.0108 mmol) and 1-phenylethanol (26 mg, 1.2128 mmol, 20 eq.) were added to a J. Young NMR tube and dissolved in C₆D₆ to give an orange solution. ¹H (600 MHz) and ³¹P{¹H} NMR spectra were measured at 10 min, 7 h and 24 h at 25 °C and were found to be identical apart from the appearance of some minor peaks in the last spectrum. In each case resonances assigned to **1** (0.005 M), **2** (0.005 M), acetophenone (0.005 M) and 1-phenylethanol (0.2 M). The reaction was repeated with wet 1-phenylethanol. In this case broad hydride resonances were also present at -20 and -21 ppm and these are thought to be associated with OsH(OH)(tmen)(PPh₃)₂ solvated with alcohol. After 6 hours the J. Young NMR tube was filled with hydrogen gas (~1 atm) and ¹H NMR spectra were obtained again immediately and after several hours. A significant decrease in the signals of **1** was observed, leaving the dihydride **2** as the major species. The signals due to the hydroxide species disappeared more slowly. The acetophenone resonance disappeared leaving only **2** and 1-phenylethanol.

(c) Observation of OsH(OCHPhMe)(tmen)(PPh₃)₂ (**3**). The toluene-d₈ solution of (b) was cooled to -80 °C and spectra were collected. The concentration of species observed are reported in the calculation in entry 3 of Table 1 (see below). **3**: ¹H NMR. -22.5 br (OsH), 0.51, 0.60, 0.87, 0.88 (br, diastereotopic Me of tmen due to chiral alkoxide), 1.42, 2.30, 4.27, 5.30 (br, four inequivalent NH), 5.18 (br, OCHMePh), 6.8-8.1 ppm (Ph). ³¹P{¹H} NMR. 25.0 (br), 13.3 ppm (br).

Hydrogenation of acetophenone using OsHCl(tmen)(PPh₃)₂ and base.

Under nitrogen, OsHCl(tmen)(PPh₃)₂ (5 mg, 0.00494 mmol), potassium tert-butoxide (10 mg, 0.0891 mmol) and acetophenone (1.000 g, 8.323 mmol) were added to a Schlenk flask resulting in an orange solution. The solution was purged with hydrogen and stirred under 1 atm hydrogen gas at room temperature for 3 h. After this time an aliquot was dissolved in CDCl₃ and the ¹H NMR spectrum was taken. Integration of the methyl peaks of acetophenone and 1-phenylethanol was used to determine a conversion of 16%.

Transfer Hydrogenation.

Under argon, OsH(NHCMe₂CMe₂NH₂)(PPh₃)₂ (13 mg, 0.01565 mmol) and acetophenone (104 mg, 0.8656 mmol) were dissolved in 2-propanol (1.005 g, 1.280 mL) and stirred in a round bottom flask. The catalyst and substrate concentrations were 0.01223 M and 0.676 M respectively giving a substrate to catalyst ratio of 55:1. An orange suspension formed due to the insolubility of the osmium complex in isopropanol. The orange suspension gradually became a yellow solution with a small amount of suspended yellow solid. After 3.5 h the reaction mixture was filtered through Celite in air and diluted to twice the volume with acetone. The sample was analyzed by GC to determine an 80 % conversion of acetophenone to 1-phenylethanol.

Preparation of racemic 1-phenylethanol-d₅.

1-Phenylethanol-d₅ was prepared by deuterating 5 mL of neat acetophenone-CD₃ catalyzed by 50 mg of RuH(NHCMe₂CMe₂NH₂)(PPh₃)₂ at 15 atm of D₂ at 25 ° C for 24 hours. The resulting mixture was then distilled at reduced pressure under argon and stored over molecular sieves. Attempts to prepare CH₃CD(OD)Ph from protio acetophenone using the same conditions resulted in deuterium scrambling into the methyl group of the product alcohol. The ¹H NMR spectrum using C₆D₆ and ²H NMR spectrum using C₆H₆ of non-deuterated 1-phenylethanol was compared to the synthesized 1-phenylethanol-d₅ to confirm that the correct protons had been labelled.

Kinetics. Concentration dependence studies.

The hydrogenation reactions were carried out in a 50 mL Parr reactor fitted with a glass sleeve and magnetic stirrer. Standard solutions of **1**, acetophenone and 1-phenylethanol in benzene were made to concentrations of 2.407 x 10⁻³ M, 0.8323 M, and 0.8210 M respectively. Stock solutions were diluted by the required amount of benzene to achieve the desired concentrations. Catalyst solutions were made up to 2 mL separately from the ketone/alcohol solutions that were made up to 3 mL, and drawn up into separate syringes. The reactor was degassed and pressurized to the desired pressure with hydrogen gas. The reactor was kept at a desired constant temperature by a Fischer Scientific Isotemp constant temperature bath. The ketone/alcohol solution was injected into the reactor under a flow of hydrogen followed by the catalyst solution, totaling 5 mL. Samples were removed at intervals by temporarily venting the reactor and drawing up a small aliquot by syringe and exposing it to air. The ratio of 1-phenylethanol to acetophenone in each aliquot was determined by GC.

Isotope effect studies.

All of the hydrogenations were carried out at constant pressures of H₂ or D₂ using a stainless steel 50 mL Parr hydrogenation reactor fitted with a glass sleeve and a magnetic stirrer. The reactor was modified such that in one of the ports a stainless steel sampling tube was added. The tubing was 30 cm in length with an inner diameter of 0.01 inches. The tube was inserted to the bottom of the reaction vessel and then secured in place using a gas-tight compression fitting. A swing valve was then attached to the other end of the sampling loop. Samples were taken during the reaction by opening the swing valve, allowing an aliquot of the reaction mixture to be sampled.² For each data point, two aliquots of equal volume were removed from the reactor, the first of which was discarded. The hydrogenation kinetic study reported above utilized a different sampling method that required the pressure in the reactor to be dropped to atmospheric pressure so that an aliquot of the reaction mixture could be extracted via syringe. Utilizing this newly developed sampling tube method the data points could be obtained at smaller time intervals and also closer to the start of the reaction with minimal changes to the pressure. As well, the new sampling method allowed for double the number of data points to be obtained leading to more accurate results. This set-up minimized the loss of precious deuterium gas. Standard solutions of catalyst, acetophenone and 1-phenylethanol in benzene were prepared by dissolving the desired amount in 10 or 5 mL volumetric flasks in an argon-filled glove box. Reaction mixtures were prepared by pipetting the appropriate amount of substrate and alcohol solutions into a 3 mL volumetric flask and catalyst solution into a 2 mL volumetric flask and diluting with benzene to give a total volume of 5 mL upon mixing. The substrate/alcohol solution and catalyst solution were taken up in a single 10 mL syringe and then injected into the reactor against a flow of gas. Samples were taken every two minutes. Concentrations of 1-

phenylethanol were determined via gas chromatography. To ensure proper stirring, a specialized neodymium stirring bar was utilized and the stirring was checked before each reaction by placing the bottom of the reactor over the stir plate to ensure proper alignment of the stir plate and stir bar. Without adequate stirring, diffusion of H₂ or D₂ into the solution does not occur as efficiently and the rate of the reaction proceeds extremely slowly.

Results

Like the ruthenium analogue RuH(NHCMe₂CMe₂NH₂)(PPh₃)₂, the new osmium amido complex **1** is an active ketone hydrogenation catalyst. With an acetophenone concentration of 0.17 M in benzene and a ratio of acetophenone to **1** of 347 to 1 and the mild conditions of 5 atm of hydrogen and 20 °C, the TOF continuously increases, reaching a maximum of 0.4 s⁻¹ with 98% conversion to 1-phenylethanol in 20 min. Under the same conditions using RuH(NHCMe₂CMe₂NH₂)(PPh₃)₂, the TOF continuously decreases from an initial maximum TOF of 1 s⁻¹, achieving 99% conversion in 20 min. (Fig. 2). The hydrido chloro complex OsHCl(tmen)(PPh₃)₂ is a precatalyst that is activated by reaction with KOtBu. This combination can be used to hydrogenate neat acetophenone to 1-phenylethanol under the mild conditions of 1 atm of dihydrogen and room temperature. Reported osmium catalysts for the hydrogenation of ketones require higher temperatures (> 80° C).¹²⁻¹⁸ An initial comparison of the kinetic behaviour of the osmium and ruthenium amido catalysts showed a distinct difference in the shape of the kinetic curves (Fig. 2). The major qualitative difference observed between the two different catalysts is that while the RuH(NHCMe₂CMe₂NH₂)(PPh₃)₂ starts with a higher rate and slows down as the reaction progresses, the osmium catalyst, **1**, displays an induction period with a relatively low rate which then increases as the reaction progresses. The decrease of the rate observed in reactions using the ruthenium catalyst is due to the increase in alcohol concentration which reacts with the catalyst to form an alkoxide complex. The decrease in available catalyst is responsible for the decrease in reaction rate. To test whether alcohol concentration was responsible for the increasing rate observed when using the osmium catalyst, **1**, the reaction was repeated with an initial concentration of 1-phenylethanol added to the reaction mixture.

Fig. 2. A comparison of the course of the hydrogenation of acetophenone using the catalysts, $\text{RuH}(\text{NHCMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$ and $\text{OsH}(\text{NHCMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$. $[\text{M}] = 4.8 \times 10^{-4} \text{ M}$, $[\text{acetophenone}]_i = 0.1665 \text{ M}$, 5 atm H_2 , $5 \text{ mL C}_6\text{H}_6$.

The addition of 1-phenylethanol to the reaction mixture resulted in a marked increase in reaction rate compared to the initial reaction with no alcohol added. In Figure 3, the plots of 1-phenylethanol concentration versus time are given for the reactions with and without alcohol. The observed induction time for the reaction without an initial concentration of alcohol has been eliminated in the reaction with alcohol added.

Fig. 3. The effect of 1-phenylethanol concentration on the rate of hydrogenation using complex **1** and acetophenone in benzene. $[\text{Os}] = 3.19 \times 10^{-4}$, $[\text{acetophenone}] = 0.1634 \text{ M}$, 5 atm H_2 , 20°C , 5 mL C_6H_6 . $[\text{1-phenylethanol}]_i = 0.1604 \text{ M}$ (grey squares), no initial 1-phenylethanol added (triangles).

In order to examine the effects of the substrate and product on the catalyst, stoichiometric reactions of the amido-hydrido complex, **1**, and the product, 1-phenylethanol, and the substrate, acetophenone, were conducted. The results were unlike those of the analogous ruthenium complex, $\text{RuH}(\text{NHCMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$, which resulted in alkoxide and enolate complexes.¹ Instead no reaction was observed between acetophenone and **1** (eq 1).

When **1** was reacted with 4 equivalents of 1-phenylethanol in C_6D_6 , as in eq 2, an equilibrium was established where some 1-phenylethanol was dehydrogenated to produce the dihydride **2**, and acetophenone. Integration of the hydride peaks of **1** and **2** in the ^1H NMR spectrum, indicate a 2:1 ratio of **1** to **2**. While the $^{31}\text{P}\{^1\text{H}\}$ signal for **1** remained sharp at 37.1 ppm, the amido peak is broadened at 29.3 ppm. The experiment was performed in a closed NMR tube which prevented any loss of hydrogen gas from **2** from leaving the system. Free hydrogen gas could not be detected in the ^1H NMR spectrum due to overlap with the methine hydrogen of 1-phenylethanol. No hydrogen is expected because the calculated concentration of acetophenone equals that of the concentration of the dihydride **2** within experimental error.

Table 1. Equilibria by adding dry 1-phenylethanol to complex **1** in benzene- d_6 or toluene- d_8 under Ar in a sealed NMR tube as observed by ^1H and ^{31}P NMR.

Entry	Equilibrium	Equation ^a	Temp. °C	$K \text{ M}^{-1}$
1	1 + ROH = 2 + AC	$K_4 = [\mathbf{2}][\text{AC}]/([\mathbf{1}][\text{ROH}]) =$ $= (0.005)(0.005)/((0.005)(0.2))$	25	0.03
2	1 + ROH = 3	$K_3 = [\mathbf{3}]/([\mathbf{1}][\text{ROH}]) = (0.005)/((0.0005)(0.2))$	-80	50
3	1 + ROH = 3	$K_3 = [\mathbf{3}]/([\mathbf{1}][\text{ROH}]) = (0.0004)/((0.005)(0.2))$	25	0.4

^a AC is acetophenone, ROH is 1-phenylethanol

When 20 equiv. of 1-phenylethanol were added to **1** in C_6D_6 or toluene- d_8 the equilibrium shifted toward the dihydride **2**, now in a ratio of 1:1 with **1**. A broad resonance of the amido hydride is shifted downfield to -23.75 ppm from -23.85 in the absence of alcohol. This is actually the weighted average of the hydride chemical shifts of the amido complex **1** at -23.85 and a small amount of the alkoxide complex $\text{OsH}(\text{OCHMePh})(\text{tmen})(\text{PPh}_3)_2$ **3** at -22.5 ppm which are in fast exchange. The last resonance can be observed when the solution is cooled to -80 °C. In fact the equilibrium shifts dramatically toward the alkoxide complex at low temperature as indicated by the equilibrium constants reported in Table 1. These were determined from the integration of proton resonances and relating these to the starting concentrations of **1** and alcohol. The alkoxide complex **3** has spectra very similar to those of $\text{RuH}(\text{OR})(\text{tmen})(\text{PPh}_3)_2$,¹ $\text{RuH}(\text{OCHMePh})(R\text{-binap})(\text{tmen})$ ¹ and $\text{RuH}(\text{OCHMePh})(R\text{-binap})((R,R)\text{-NH}_2\text{CHPhCHPhNH}_2)$ ¹⁹ reported previously. The reaction of the osmium amido complex with water to produce a hydride hydroxide complex $\text{OsH}(\text{OH})(\text{tmen})(\text{PPh}_3)_2$ has also been reported but this is only observed when the added alcohol contains water.²⁰

The ability of **1** to dehydrogenate 1-phenylethanol implied its activity as a transfer hydrogenation catalyst. To test its effectiveness as a transfer hydrogenation catalyst, **1** and acetophenone were stirred in 2-propanol under argon in a ratio of 55:1. After a period of 3.5 h, 80 % conversion of acetophenone to 1-phenylethanol was achieved with a TOF of 13 h^{-1} . It is of note that this is much slower than the TOF of 0.4 s^{-1} achieved for the preliminary H_2 -hydrogenation described above (Figures 2 and 3). Turnover frequencies of 120 and 60 h^{-1} were achieved for the transfer hydrogenation of acetophenone using $\text{OsH}_2\text{Cl}_2(\text{P}^i\text{Pr}_3)_2$ and $\text{OsH}_2\text{Cl}_2(\text{PMe}^t\text{Bu}_2)_2$ respectively as catalysts in Werner's group.¹⁷ Although both reported TOF are higher, it should be noted that they performed their reactions at 83°C while we, at room temperature.

Kinetics.

Kinetic experiments were performed to determine the effect of the catalyst, substrate, and hydrogen concentrations on the rate of hydrogenation of acetophenone to 1-phenylethanol using **1** as a catalyst. Previous results from preliminary hydrogenation experiments using **1** indicated that the rate of hydrogenation was increased by the presence of the product alcohol (Fig. 3). Therefore kinetic experiments were needed with an alcohol present at the start. The fact that **1** is also a transfer hydrogenation catalyst precluded the use of 2-propanol as a solvent due to competing transfer and H₂-hydrogenation processes. Instead, the kinetic experiments were performed in benzene as the solvent and nearly equal concentrations of the substrate, acetophenone, and the product, 1-phenylethanol, were added before beginning the hydrogenation. The faster alcohol-assisted rate (Table 2) was thereby achieved throughout the hydrogenation and any transfer hydrogenation from 1-phenylethanol to acetophenone had no net effect on the concentration of the substrate or product.

Table 2. Dependence of the rate of production of alcohol catalyzed by **1** on the concentrations of **1**, H₂, acetophenone, and temperature.^a

Run	[1], M	Pressure H ₂ , atm; [H ₂], M	[Ketone], M	Temp.	r, rate, Ms ⁻¹	k=r/([Os][H ₂]), M ⁻¹ s ⁻¹
1	9.6×10 ⁻⁵	5.0; 1.32×10 ⁻²	0.1665	293	4.6×10 ⁻⁵	36
2	4.8×10 ⁻⁵	5.0; 1.32×10 ⁻²	0.1665	293	2.1×10 ⁻⁵	33
3	1.4×10 ⁻⁴	5.0, 1.32×10 ⁻²	0.1665	293	8.3×10 ⁻⁵	45
4	9.6×10 ⁻⁵	5.0, 1.32×10 ⁻²	0.1332	293	4.5×10 ⁻⁵	36
5	9.6×10 ⁻⁵	5.0, 1.32×10 ⁻²	0.1998	293	5.8×10 ⁻⁵	46
6	1.4×10 ⁻⁴	2.0, 5.28×10 ⁻³	0.1665	293	4×10 ⁻⁵	26
7	1.4×10 ⁻⁴	5.0, 1.32×10 ⁻²	0.1665	293	6.0×10 ⁻⁵	32
8	1.4×10 ⁻⁴	9.0, 2.38×10 ⁻²	0.1665	293	9×10 ⁻⁵	26
9	1.4×10 ⁻⁴	14.0, 3.8×10 ⁻²	0.1665	293	10×10 ⁻⁵	26
10 ^b	2.7×10 ⁻⁴	5.0, 1.32×10 ⁻²	0.1665	293	9.3×10 ⁻⁵	26
11 ^b	2.7×10 ⁻⁴	5.0, 1.36×10 ⁻²	0.1665	298	1.03×10 ⁻⁴	28
12 ^b	2.7×10 ⁻⁴	5.0, 1.39×10 ⁻²	0.1665	303	1.16×10 ⁻⁴	31
13 ^b	2.7×10 ⁻⁴	5.0, 1.24×10 ⁻²	0.1665	288	7.4×10 ⁻⁵	22
14 ^b	2.7×10 ⁻⁴	5.0; 1.19×10 ⁻²	0.1665	283	6.1×10 ⁻⁵	19

^a Initial [1-phenylethanol] = 0.164 M

^b Temperature varied; different set up and catalyst batch.

The effect of the catalyst concentration on the rate of the reaction can be seen in Figure 4. As the concentration of **1** is increased, keeping the hydrogen pressure and initial substrate and alcohol concentrations constant, the rate of hydrogenation increases proportionally.

Fig. 4. The effect of osmium concentration on the initial rate of acetophenone hydrogenation (runs 1, 2 and 3 in Table 2). $[1\text{-phenylethanol}]_i = 0.1642\text{ M}$, 5 atm H_2 , $[\text{Acetophenone}]_i = 0.1665\text{ M}$, $5\text{ mL C}_6\text{H}_6$. Molar osmium concentrations are given in the legend.

When the concentration of **1** and the initial concentration of product, along with the pressure of hydrogen were kept constant and the substrate concentration was varied, no change in the rate of hydrogenation was observed. The straight lines observed in all the kinetic experiments, reinforces the fact that there is no dependence on the substrate concentration. The linearity also means that, although the presence of alcohol increases the rate of reaction compared to the rate of reaction in the absence of alcohol, the reaction is not directly dependent on the concentration of the alcohol. This is consistent with the observation of constant rate to complete conversion. Varying the hydrogen pressure (and thereby the hydrogen concentration) and keeping the catalyst concentration and the initial substrate and alcohol concentrations constant caused an increased rate of hydrogenation with higher hydrogen pressures (Fig. 5). The hydrogen concentration dependence is more complicated than that of previously reported ruthenium systems. At pressures lower than 5 atm we assume that the rate is first order in hydrogen concentration but that at higher pressures another step becomes rate determining and the hydrogen pressure dependence levels off.

Fig. 5. The effect of hydrogen concentration on the initial rate of acetophenone hydrogenation (runs 6, 7, and 8 in Table 2). $[\text{Os}] = 1.44 \times 10^{-4} \text{ M}$, $[\text{acetophenone}]_i = 0.1665 \text{ M}$, $[\text{1-phenylethanol}]_i = 0.1642 \text{ M}$, 5 mL C_6H_6 . Hydrogen pressures 2, 5, 9 and 14 atm, respectively.

Thus the rate law for the alcohol-assisted hydrogenation of acetophenone using **1** as a catalyst at up to 5 atm H_2 is given by eq 3.

$$\text{Rate} = d[\text{1-phenylethanol}]/dt = -d[\text{acetophenone}]/dt = k[\mathbf{1}][\text{H}_2]. \quad (3)$$

At a temperature of 20°C a rate constant k of $34 \text{ M}^{-1}\text{s}^{-1}$ was obtained. By contrast the analogous ruthenium complex has the same rate law with k of $1.1 \times 10^2 \text{ s}^{-1}$.¹ Thus the Ru complex is three times more active under comparable conditions. The temperature dependence (and isotope effect studies) were determined using a different reactor set up and batch of catalyst. The rate constant in this case was $26 \text{ M}^{-1}\text{s}^{-1}$ at 293 K. The Eyring plot (Fig. 6) used five rates from temperatures spaced five degrees apart from 10°C to 30°C. The thermodynamic values for activation enthalpy and entropy are $\Delta H^\ddagger = 3.7 \text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger = -39 \text{ cal}\cdot\text{mol}^{-1}$ with a Gibbs's free energy of activation of $\Delta G^\ddagger$ (293 K) = $15 \text{ kcal}\cdot\text{mol}^{-1}$.

Fig. 6. An Eyring plot for temperatures ranging from 283 K to 303 K (runs 10 – 14 in Table 1).

The values correspond to a transition state that is more ordered than the reactants due to the loss of entropy of the gaseous hydrogen.

Isotope effect measurements.

The rate data to probe isotope effects were collected in at least triplicate to improve the accuracy of the data (Table 3). The error in the rates is 10%. The experiments requiring deuterium gas were measured at 5 atm D_2 pressure. A few runs gave a value that deviated by more than 10%, probably because of leak or impurity, were rejected. The purity of the catalyst was verified weekly by ^1H and ^{31}P NMR and by the standard rate generated by the all protio system.

In order to differentiate between the protio and deuterio gas, acetophenone and 1-phenylethanol for each run, a three letter designation code was used such that the first letter of the code represents the gas, the second letter the ketone and the third letter the alcohol that was used in the experiment. H is used for protio species, while D is used for deuterio species. For example, a set of runs that used H_2 gas, protio acetophenone and protio 1-phenylethanol would be designated HHH.

A typical comparison of plots for the HHH and DDD runs is shown in Fig. 7. The slight delay in the first 60 seconds is likely to be associated with temperature changes when the solution is added to the reactor and dissolution of gas into the solution, slower for deuterium. The lower initial pressure of gas allows the reverse of reaction 4, the dehydrogenation/dedeuteration of the added alcohol, to occur, resulting in an initial drop in alcohol concentration.

Table 3. Average initial reaction rates, rate constants, k , and the isotope effects using catalyst **1**. Runs were carried out using a single syringe in which the catalyst, substrate and alcohol were mixed prior to injection into the reactor. $[\text{Os}] = 3.18 \times 10^{-4} \text{ M}$, [acetophenone] or [acetophenone- d^3] = 0.163 M, [1-phenylethanol] or [1-phenylethanol- d^5] = 0.160 M, 5 atm of H_2 or $\text{D}_2 = 1.32 \times 10^{-2} \text{ M}$, 20°C , 5 mL C_6H_6 .

Kinetic run H* ₂ /PhCOCH* ₃ /ROH*	Rate of reaction, v ₀	Rate constant k	Isotope effect (k _H /k _D)
	(10 ⁻⁵ Ms ⁻¹)	k = v ₀ /([Os][H ₂]) (M ⁻¹ s ⁻¹)	
HHH	11±1	26	
HHD	11±1	26	1.0±0.1
HDD	11±1	26	1.0±0.1
DDD	10±1	24	1.1±0.1

Figure 7. Sample plot of the HHH (squares) and DDD (circles) runs. The error bars represent one standard deviation.

Discussion

The rate law for the hydrogenation of acetophenone catalyzed by **1** in the presence of excess product alcohol with pressures less than 5 atm displays a dependence on the concentration of catalyst and the concentration of hydrogen. This indicates that the rate limiting step involves the addition of hydrogen to the catalyst, a feature similar to the system using the ruthenium hydridoamido complex $\text{RuH}(\text{NHCM}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$ as a catalyst.¹ What is not taken into

account is the effect of alcohol on the rate. At relatively low concentrations of alcohol (ca. < 0.02 M), the rate of hydrogenation is slower than that when higher concentrations of alcohol are present (ca. > 0.02 M) (Fig. 3). Yet at higher alcohol concentrations, the rate of hydrogenation is independent of alcohol concentration. The alcohol is changing the nature of the rate limiting step in such a way as to lower the activation energy of that transition state. At low concentrations of alcohol the hydrogenation reaction operates by a slow mechanism and at higher concentrations of alcohol it operates by a faster “alcohol-assisted” mechanism. The non-alcohol-assisted mechanism (**I** in Scheme 1) is the same as that proposed for the analogous ruthenium system,¹ where hydrogen is heterolytically split across a metal amido bond generating a metal hydride and amine. The alcohol-assisted mechanism (**II** in Scheme 1) involves a six-membered ring consisting of the metal center, a molecule of hydrogen, the O-H of a molecule of alcohol, and the amido nitrogen (Fig. 1). Rather than splitting hydrogen directly across the osmium-amido bond, the hydrogen is split between the metal and alcohol oxygen, while the amido nitrogen is protonated by the alcohol proton. This proton shuttle mechanism is proposed to facilitate the addition of hydrogen to the catalyst thereby raising the rate of hydrogenation. This alcohol effect was not observed for the related ruthenium system,¹ and this likely reflects the higher reactivity of the ruthenium-nitrogen(amido) bond compared to the Os-N bond toward dihydrogen and other small molecules.^{9; 21}

Scheme 1. A possible mechanism for the hydrogenation of acetophenone to 1-phenylethanol using $\text{OsH}(\text{NHCMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$ as a catalyst: the non-assisted splitting of dihydrogen (**I**) and the alcohol-assisted splitting of dihydrogen (**II**).

The observed kinetic isotope effects (KIE) are negligible or small, with a value of 1.1 ± 0.1 for the DDD system, comparing the all protio system with the system using deuterium gas, deuterated acetophenone (at the methyl) and deuterated alcohol (except for the phenyl group) (Table 3). Deuteration of the gas and substrate does not seem to significantly affect the rates (the DDH and DHH systems have KIE of 1.0 ± 0.1). The value of 1.1 contrasts with the ruthenium system *trans*- $\text{RuH}_2(\text{tmen})(\text{binap})$ which has a $k_{\text{H}}/k_{\text{D}}$ of 2.1 ± 0.1 for the direct heterolytic splitting of dihydrogen/dideuterium across the ruthenium-nitrogen(amido) bond in benzene.² The proton shuttle mechanism like that shown in Scheme 1 appears to lack a KIE. Density functional theory is currently being applied to further interpret this result and understand this mechanism more deeply.

NMR experiments to examine the reaction of alcohol with complex **1** have revealed several details. The triplet hydride resonance of the dihydride **2** in the presence of alcohol is broadened to a peak width of 18 Hz at 600 MHz at 25 °C. This is attributed to the formation of an $\text{OsH} \cdots \text{HOR}$ dihydrogen bond (hydridic protonic interaction) as shown in **2·ROH** in Scheme 2; this causes a shortening of the T_1 and broadening of the hydride resonance²²⁻²⁹ A detail still to be determined

is the route followed when **1** reacts with alcohol to give the dihydride **2** and the alkoxide **3** (Scheme 2). This is the equivalent question, discussed in the literature, as to whether such dihydride complexes react with acetophenone to give directly the alcohol and the amido complex **1** via H^+/H^- transfer to the ketone in the transition state (path 2 to a polarized TS, then path 3 to **1**, and then path 4 to the alkoxide complex **3** of Scheme 2)^{1; 2; 4; 5; 7; 30} or to give an alkoxide complex **3** via an initial hydride transfer (path 2 to an ion pair TS that includes a hydrogen-bonded alkoxide, then path 5 to **3** in Scheme 2).^{19; 31-36} Arguments have been made for each pathway depending on the solvent and other conditions. An observation in the current work is that the alkoxide forms quickly from the amido complex and alcohol and is more prevalent at low temperatures. In the low dielectric constant solvent benzene, hydride transfer from **2** to acetophenone to give a transient free alkoxide seems unfavorable, making a concerted H^+/H^- transfer route more likely as proposed previously for catalysts operating in benzene/alcohol mixtures.

Scheme 2. Routes to explain the formation of the alkoxide complex **3**.

Conclusions

The synthesis of the aminoamido complex of osmium OsH(NHCMe₂CMe₂NH₂)(PPh₃)₂ has allowed a detailed study of the (base-free) hydrogenation of acetophenone in benzene catalyzed by this well-defined complex. This osmium complex can split dihydrogen across its metal-amido bond to produce a *trans*-dihydride **2** and this behaviour is somewhat analogous to

the ruthenium complex $\text{RuH}(\text{NHCMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$. Where the osmium complex differs from the ruthenium complex is in the reactivity of the amido nitrogen. Stronger bonding between osmium and the amido nitrogen makes it less reactive than the ruthenium counterpart.⁹ The osmium amido complex can act as a transfer hydrogenation catalyst as well as an H_2 -hydrogenation catalyst. It acts most efficiently as a direct hydrogenation catalyst for acetophenone when alcohol is present.

The kinetic isotope effect has been determined experimentally for the homogeneous hydrogenation of ketones using $\text{OsH}(\text{NHCMe}_2\text{CMe}_2\text{NH}_2)(\text{PPh}_3)_2$ (**1**) and found to be about 1.1 ± 0.1 . The next step will be to use DFT calculations to assist in finding a mechanism that explains the lower KIE for osmium than the value of 2.1 found for the related ruthenium system $\text{RuH}_2(\text{NH}_2\text{CMe}_2\text{CMe}_2\text{NH}_2)(R\text{-binap})$.

Acknowledgements

Funding was provided by a Discovery grant to RHM from NSERC and Deutscher Akademischer Austauschdienst (DAAD) to KM.

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Supporting Material for **Alcohol Assisted Base-free Hydrogenation of Acetophenone
Catalyzed by OsH(NHCMe₂CMe₂NH₂)(PPh₃)₂**

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Figure 1. Reaction coordinate diagram for the hydrogenation of acetone using A as a catalyst. The solid line represents no alcohol assistance and heterolytic cleavage via a four membered transition state, C*. The dashed line represents isopropanol assisted H_2 splitting via a six membered transition state J*.

Average reaction rates, reaction constants, k, and the isotope effects using catalyst batch A.

Table 1. Average reaction rates, reaction constants, k, and the isotope effects using catalyst batch A. Runs 1 and 2 were carried out using separate syringes for the catalyst and substrate/alcohol mixtures. $[\text{Os}] = 3.18 \times 10^{-4} \text{ M}$, $[\text{acetophenone}] = 0.1634 \text{ M}$, 5 atm of H_2 or $\text{D}_2 = 1.32 \times 10^{-2} \text{ M}$, 20°C , 5 mL C_6H_6 .

Kinetic run	Rate of reaction, v_0 (10^{-5} Ms^{-1})	Rate constant k $k = v_0/([\text{Os}][\text{H}_2])$ ($\text{M}^{-1}\text{s}^{-1}$)	Isotope effect ($k_{\text{H}}/k_{\text{D}}$)
HHH			
Run 1	14.17	33.66	
Run 2	13.15	31.23	
Average	13.66	32.45	
Standard deviation	0.72	1.72

Figure 2. Plot of the average values of conversion from runs 1 and 2, which refer to HHH conditions. Two syringes were used to inject the reactants. The error bars shown represent one standard deviation.

Average reaction rates, reaction constants, k, and the isotope effects using catalyst batch B.

Table 1. Average initial reaction rates, rate constants, k, and the isotope effects using catalyst batch B. Runs 3-17 were carried out using a single syringe in which the catalyst, substrate and alcohol were mixed prior to injection into the reactor. $[\text{Os}] = 3.18 \times 10^{-4} \text{ M}$, [acetophenone] or [acetophenone- d^3] = 0.1634 M, [1-phenylethanol] or [1-phenylethanol- d^5] = 0.1604 M, 5 atm of H_2 or $\text{D}_2 = 1.32 \times 10^{-2} \text{ M}$, 20°C , 5 mL C_6H_6 .

Kinetic run	Initial Rate of Reaction, v_0 (10^{-5} Ms^{-1})	Rate Constant, k $k = v_0/([\text{Os}][\text{H}_2])$ ($\text{M}^{-1}\text{s}^{-1}$)	Isotope Effect ($k_{\text{HHH}}/k_{\text{XYZ}}$)
HHH			
Run 3	14.27	33.89	
Run 4	18.87	44.82	
Average	16.57	39.36	
Standard deviation	3.26	7.73	
DDD			
Run 5	11.85	28.15	
Run 6	15.47	36.73	
Run 7	12.74	30.25	
Run 8	12.77	30.32	
Run 9	13.27	31.50	
Average	12.67	31.39	$\frac{k_{\text{HHH}}}{K_{\text{DDD}}} = 1.3$
Standard deviation	1.36	3.22	0.2
HHD			
Run 10	15.70	37.28	
Run 11	14.34	34.07	
Run 12	17.11	40.63	
Run 13	14.31	33.97	
Run 14	13.00	30.86	
Average	13.97	35.36	$\frac{k_{\text{HHH}}}{K_{\text{HHD}}} = 1.1$
Standard deviation	1.57	3.72	0.2
HDD			
Run 15	13.47	31.99	
Run 16	15.54	36.91	

Run 17	14.34	34.06	
Average	14.45	34.32	$\frac{k_{HHH}}{K_{HDD}} = 1.1$
Standard deviation	1.04	2.47	0.1

Figure 1. Sample plot of the average values of conversion from runs 3 and 4 (HHH) and runs 5,6, 7, 8, 9 (DDD). The one syringe method was used for all of the runs shown in the plot. The error bars represent one standard deviation.

Average reaction rates, reaction constants, k, and the isotope effects using catalyst batch C.

Table 1. Average initial reaction rates, rate constants, k, and the isotope effects using catalyst batch C. Runs 18-25 were carried out using a single syringe in which the catalyst, substrate and alcohol were mixed prior to injection into the reactor. $[\text{Os}] = 3.18 \times 10^{-4} \text{ M}$, $[\text{acetophenone}]$ or $[\text{acetophenone-d}^3] = 0.1634 \text{ M}$, $[\text{1-phenylethanol}]$ or $[\text{1-phenylethanol-d}^5] = 0.1604 \text{ M}$, 5 atm of H_2 or $\text{D}_2 = 1.32 \times 10^{-2} \text{ M}$, 20°C , 5 mL C_6H_6 .

Kinetic run	Initial Rate of Reaction, v_0 (10^{-5} Ms^{-1})	Rate Constant, k $k = v_0/([\text{Os}][\text{H}_2])$ ($\text{M}^{-1}\text{s}^{-1}$)	Isotope Effect ($k_{\text{HHH}}/k_{\text{XYZ}}$)
HHH			
Run 18	17.70	42.03	
Run 19	17.62	41.85	
Average	17.66	41.94	
Standard deviation	0.06	0.13	
DDH			
Run 20	18.74	44.50	
Run 21	16.99	40.34	
Run 22	20.51	48.72	
Run 23	17.62	41.84	
Average	18.46	43.85	$\frac{k_{\text{HHH}}}{K_{\text{DDH}}} = 1.0$
Standard deviation	1.55	3.67	0.1
DHH			
Run 24	12.73	30.22	
Run 25	16.01	38.02	
Average	14.37	34.12	$\frac{k_{\text{HHH}}}{K_{\text{DHH}}} = 1.1$
Standard deviation	2.32	5.51	0.2

Coordinates of A:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	76	0	-0.126341	-0.018624	0.118112
2	7	0	1.667789	1.198579	0.402428
3	7	0	1.318831	-1.286441	-0.369890
4	15	0	-1.501310	1.733273	-0.304397
5	15	0	-1.744267	-1.560625	-0.058152
6	6	0	2.704426	-0.911634	-0.175746
7	6	0	2.793292	0.591647	-0.346094
8	1	0	-0.624342	0.302281	1.617530
9	1	0	1.552432	2.172388	0.144926
10	1	0	1.857355	1.177032	1.400136
11	1	0	1.208020	-2.284534	-0.487888
12	1	0	-0.882525	2.992403	-0.575711
13	1	0	-2.333975	1.734405	-1.460329
14	1	0	-2.499267	2.282055	0.561459
15	1	0	-1.381679	-2.878833	-0.465602
16	1	0	-2.507778	-1.954923	1.074142
17	1	0	-2.848445	-1.434132	-0.949163
18	1	0	3.080670	-1.190078	0.824072
19	1	0	3.369144	-1.390200	-0.906544
20	1	0	2.644911	0.843741	-1.397766
21	1	0	3.758417	0.989061	-0.014282

Sum of electronic and thermal Energies= -967.500525
Sum of electronic and thermal Enthalpies= -967.499581
Sum of electronic and thermal Free Energies= -967.549752

Coordinates of B:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	-0.025914	0.028873	-1.548918
2	1	0	-0.229001	-0.374947	1.861325
3	7	0	1.595131	-1.372851	-0.032457
4	1	0	1.558306	-2.163821	0.600176
5	1	0	1.575777	-1.747884	-0.974163
6	7	0	1.515256	1.359995	0.093264
7	1	0	1.305785	2.205613	-0.424632
8	1	0	0.124055	0.396599	1.828733
9	15	0	-1.724709	-1.622574	-0.194674
10	1	0	-1.338916	-2.907221	-0.679235
11	1	0	-2.590568	-2.131983	0.815155
12	1	0	-2.750509	-1.420105	-1.158014
13	15	0	-1.601950	1.686277	-0.073576
14	1	0	-1.100298	2.945783	-0.500665

15	1	0	-2.685755	1.616022	-0.988519
16	1	0	-2.357805	2.181226	1.024375
17	6	0	2.665719	0.733559	-0.513981
18	1	0	2.570328	0.550980	-1.604919
19	1	0	3.580870	1.328155	-0.370865
20	6	0	2.851873	-0.605523	0.161855
21	1	0	2.975242	-0.448920	1.235788
22	1	0	3.713001	-1.161194	-0.223190
23	76	0	-0.122408	-0.006986	0.089716

Sum of electronic and thermal Energies= -968.662015
Sum of electronic and thermal Enthalpies= -968.661071
Sum of electronic and thermal Free Energies= -968.713046

Coordinates of B_{P1_N1}:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	76	0	-0.120407	-0.006832	0.088207
2	1	0	-0.022507	0.051946	-1.549183
3	1	0	-0.089960	-0.408214	1.858848
4	7	0	1.592078	-1.370914	-0.082146
5	1	0	1.551509	-2.188403	0.515447
6	1	0	1.572929	-1.704426	-1.039367
7	7	0	1.518622	1.352074	0.138061
8	1	0	1.318589	2.219947	-0.345727
9	1	0	-0.002522	0.434256	1.831568
10	15	0	-1.727863	-1.618314	-0.171460
11	1	0	-1.356561	-2.895520	-0.686905
12	1	0	-2.556836	-2.146772	0.860976
13	1	0	-2.789902	-1.409293	-1.094371
14	15	0	-1.609566	1.680647	-0.092608
15	1	0	-1.111373	2.943683	-0.512597
16	1	0	-2.673984	1.596166	-1.028091
17	1	0	-2.389765	2.170155	0.989736
18	6	0	2.672339	0.745941	-0.482920
19	1	0	2.585058	0.601865	-1.580374
20	1	0	3.587629	1.333068	-0.312544
21	6	0	2.850450	-0.616431	0.146966
22	1	0	2.966886	-0.497444	1.226467
23	1	0	3.711565	-1.161954	-0.252310

Sum of electronic and thermal Energies= -968.663021
Sum of electronic and thermal Enthalpies= -968.662076
Sum of electronic and thermal Free Energies= -968.712496

Coordinates of B_{NH2}:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	76	0	-0.123282	-0.006990	0.085693
2	7	0	1.575684	-1.366968	-0.169469
3	7	0	1.519044	1.332752	0.223745
4	15	0	-1.719093	-1.630210	-0.131701
5	15	0	-1.594980	1.700143	-0.130235
6	6	0	2.676322	0.762006	-0.423206
7	6	0	2.838858	-0.640769	0.117083
8	1	0	3.593809	1.329817	-0.205457
9	1	0	2.947556	-0.594287	1.202955
10	1	0	3.697461	-1.166944	-0.312359
11	1	0	-0.268819	0.387046	1.830731
12	1	0	0.122207	-0.370904	1.843968
13	1	0	1.525661	-2.224977	0.367341
14	1	0	1.554735	-1.628762	-1.148634
15	1	0	-0.029472	0.093908	-1.551262
16	1	0	1.335166	2.236304	-0.197600
17	1	0	-1.330909	-2.925869	-0.587621
18	1	0	-2.542195	-2.123482	0.924890
19	1	0	-2.787140	-1.485396	-1.061167
20	1	0	-1.055881	2.987442	-0.397238
21	1	0	-2.536643	1.679318	-1.189805
22	1	0	-2.500410	2.110594	0.883303
23	1	0	2.601259	0.690520	-1.528874

Sum of electronic and thermal Energies= -968.661993
Sum of electronic and thermal Enthalpies= -968.661049
Sum of electronic and thermal Free Energies= -968.712772

Coordinates of B_{P1_P2}:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	76	0	-0.132182	-0.006498	0.085747
2	7	0	1.572889	-1.375899	-0.097926
3	7	0	1.514103	1.346932	0.161604
4	15	0	-1.701547	-1.652996	-0.161961
5	15	0	-1.567146	1.727410	-0.102776
6	6	0	2.666725	0.742680	-0.463933
7	6	0	2.835477	-0.632011	0.143304
8	1	0	2.582158	0.616301	-1.563973
9	1	0	3.586013	1.320203	-0.282222
10	1	0	2.953598	-0.532693	1.224798
11	1	0	3.693452	-1.175543	-0.265211
12	1	0	-0.508862	0.010765	1.861098
13	1	0	0.331539	0.017703	1.842050
14	1	0	1.525916	-2.201419	0.488067
15	1	0	1.551815	-1.695081	-1.059957
16	1	0	-0.057060	0.056118	-1.551958

17	1	0	1.319933	2.221759	-0.312118
18	1	0	-1.263194	-2.966192	-0.509014
19	1	0	-2.616033	-2.094889	0.839029
20	1	0	-2.677228	-1.567188	-1.193206
21	1	0	-0.993751	3.001012	-0.365414
22	1	0	-2.526846	1.750471	-1.147110
23	1	0	-2.447364	2.155032	0.927447

Sum of electronic and thermal Energies= -968.661956
Sum of electronic and thermal Enthalpies= -968.661012
Sum of electronic and thermal Free Energies= -968.711587

Coordinates of C*:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	76	0	0.136851	-0.000276	0.019964
2	7	0	-1.573911	-1.342612	0.273630
3	7	0	-1.573392	1.364341	-0.199767
4	6	0	-2.757264	-0.758583	-0.305260
5	6	0	-2.837093	0.681908	0.161451
6	15	0	1.667890	-1.641955	-0.081345
7	15	0	1.703646	1.628520	0.018234
8	1	0	0.206571	0.041593	-1.641085
9	1	0	-0.189454	-0.134821	1.800064
10	1	0	-0.876839	-0.743469	1.354148
11	1	0	-3.675645	-1.275661	0.007990
12	1	0	-2.733214	-0.768144	-1.409801
13	1	0	-2.917524	0.704996	1.250717
14	1	0	-3.703253	1.197147	-0.264716
15	1	0	-1.578217	1.605029	-1.184023
16	1	0	-1.480895	2.228476	0.321840
17	1	0	1.313862	2.953494	-0.341922
18	1	0	2.433285	2.017396	1.178662
19	1	0	2.835081	1.581051	-0.844431
20	1	0	2.787685	-1.520634	-0.946576
21	1	0	2.397741	-2.134262	1.038199
22	1	0	1.240049	-2.916966	-0.546302
23	1	0	-1.435685	-2.304803	0.002453

Sum of electronic and thermal Energies= -968.647203
Sum of electronic and thermal Enthalpies= -968.646259
Sum of electronic and thermal Free Energies= -968.697036

Coordinates of D:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.788475	-0.684105	0.325142

2	6	0	2.788241	0.684136	-0.326093
3	7	0	1.561016	-1.392684	-0.067400
4	7	0	1.560993	1.392633	0.067252
5	15	0	-1.686852	-1.614539	-0.034869
6	15	0	-1.686691	1.614649	0.034232
7	1	0	1.634055	-1.743758	-1.014978
8	1	0	1.399502	-2.179561	0.549296
9	1	0	1.634565	1.743559	1.014846
10	1	0	1.399104	2.179614	-0.549221
11	1	0	-0.009668	-0.064647	1.712060
12	1	0	3.693894	-1.236506	0.050784
13	1	0	2.764120	-0.575733	1.412140
14	1	0	3.693805	1.236575	-0.052286
15	1	0	2.763201	0.575785	-1.413077
16	1	0	-2.646558	-1.786376	1.004837
17	1	0	-1.240837	-2.972513	-0.031111
18	1	0	-2.618410	-1.785487	-1.100826
19	1	0	-2.614801	1.790874	1.102367
20	1	0	-2.649706	1.781546	-1.003185
21	1	0	-1.240546	2.972546	0.022640
22	1	0	-0.010346	0.064596	-1.711538
23	76	0	-0.140297	-0.000026	0.000310

Sum of electronic and thermal Energies= -968.677615
Sum of electronic and thermal Enthalpies= -968.676670
Sum of electronic and thermal Free Energies= -968.728194

Coordinates of E:

Coordinates of F*:

Coordinates of G:

Coordinates of H:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	76	0	0.023010	-0.038209	0.064617
2	7	0	0.154496	0.081947	2.199697
3	7	0	2.196713	0.043784	0.353242
4	15	0	0.103338	0.177551	-2.212740
5	15	0	-2.224830	0.103464	0.157094
6	6	0	2.504588	-0.113400	1.798504
7	6	0	1.444803	0.642117	2.572476
8	6	0	-0.880700	-2.995861	3.574108
9	8	0	0.243275	-2.484620	2.900528
10	1	0	-1.803115	-2.709882	3.036081

11	1	0	2.500752	0.960180	0.038932
12	1	0	0.057104	1.602792	0.091589
13	1	0	0.127574	-1.489196	2.732492
14	1	0	-0.568702	0.688296	2.575093
15	1	0	2.711472	-0.640331	-0.191924
16	1	0	1.318096	0.606014	-2.818488
17	1	0	-0.152881	-0.855489	-3.153405
18	1	0	-0.717271	1.149884	-2.839212
19	1	0	-2.793246	0.565824	1.373156
20	1	0	-2.933667	0.979206	-0.703804
21	1	0	-3.083658	-1.013961	-0.008875
22	1	0	1.535552	1.719005	2.339894
23	1	0	1.643157	0.522726	3.648508
24	1	0	3.517821	0.237208	2.024418
25	1	0	2.431995	-1.178080	2.036044
26	1	0	0.125707	-1.817744	-0.247670
27	1	0	0.034010	-1.782716	0.591181
28	6	0	-0.782255	-4.513688	3.564320
29	1	0	0.123624	-4.831964	4.089900
30	1	0	-1.647293	-4.972115	4.053404
31	1	0	-0.724807	-4.883701	2.537370
32	6	0	-0.978007	-2.446956	4.997006
33	1	0	-1.036570	-1.354576	4.986289
34	1	0	-1.864660	-2.830566	5.513476
35	1	0	-0.090467	-2.733114	5.570386

Sum of electronic and thermal Energies= -1162.795070
Sum of electronic and thermal Enthalpies= -1162.794126
Sum of electronic and thermal Free Energies= -1162.863138

Coordinates of J*:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	76	0	0.869187	0.003299	-0.043753
2	15	0	1.098039	-2.036900	-0.979699
3	1	0	0.601211	-3.227408	-0.384374
4	1	0	0.510068	-2.240964	-2.258384
5	1	0	2.382535	-2.544977	-1.308526
6	15	0	2.690000	-0.257541	1.297297
7	1	0	2.703886	-1.018086	2.498374
8	1	0	3.886483	-0.801022	0.760221
9	1	0	3.293706	0.903651	1.859408
10	1	0	0.433358	2.222217	1.523183
11	7	0	0.512402	2.096744	0.520491
12	1	0	1.315735	2.633947	0.214784
13	1	0	-1.572692	2.218477	0.431092
14	6	0	-0.720668	2.597967	-0.139030
15	1	0	-0.740037	3.691371	-0.159973
16	1	0	-1.718136	2.325663	-2.011302
17	6	0	-0.785757	2.008316	-1.530703
18	1	0	0.054734	2.357153	-2.140749

19	1	0	-0.705932	0.105231	-2.285395
20	7	0	-0.736574	0.551466	-1.376955
21	1	0	-1.647269	0.249282	-0.769052
22	8	0	-2.468849	0.146837	0.360877
23	6	0	-3.436506	-0.822917	0.542262
24	1	0	-2.976448	-1.831704	0.636453
25	6	0	-4.207434	-0.568958	1.838127
26	1	0	-4.958630	-1.342671	2.029885
27	1	0	-4.711689	0.400894	1.782626
28	1	0	-3.516897	-0.540320	2.684667
29	6	0	-4.399864	-0.889495	-0.647028
30	1	0	-5.160989	-1.666529	-0.518163
31	1	0	-3.854178	-1.101026	-1.571465
32	1	0	-4.904920	0.074215	-0.767172
33	1	0	-0.776088	-0.317272	0.878955
34	1	0	-0.116444	-0.616132	1.340910
35	1	0	1.921188	0.570234	-1.178282

Sum of electronic and thermal Energies=	-1162.929670
Sum of electronic and thermal Enthalpies=	-1162.928725
Sum of electronic and thermal Free Energies=	-1162.995684

Coordinates of K:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	0.054541	0.069770	-0.023468
2	7	0	-0.014217	-0.055962	2.759258
3	15	0	3.246933	-0.009285	3.051563
4	15	0	3.294083	0.131579	-0.181158
5	6	0	-1.247195	-0.292720	1.984398
6	6	0	-1.163624	0.486519	0.688952
7	6	0	0.231025	-4.093429	-0.496828
8	8	0	-0.095187	-2.789597	-0.041876
9	1	0	-0.055148	0.840289	3.229952
10	1	0	1.600798	1.675218	1.459840
11	1	0	-0.093409	-0.846043	-0.450486
12	1	0	0.267893	0.735179	-0.756476
13	1	0	0.094364	-0.773486	3.465353
14	1	0	2.796828	0.162031	4.396241
15	1	0	4.108456	-1.107159	3.340597
16	1	0	4.264769	0.984161	3.120737
17	1	0	2.876415	0.485110	-1.500136
18	1	0	4.346014	1.088477	-0.104386
19	1	0	4.127722	-0.950145	-0.592583
20	1	0	-1.076698	1.555236	0.898673
21	1	0	-2.065654	0.317203	0.091348
22	1	0	-2.143725	-0.011620	2.546922
23	1	0	-1.295903	-1.359904	1.758777
24	1	0	1.673401	-1.755579	1.415192
25	1	0	0.648930	-2.435911	0.509529

26	1	0	0.494016	-4.714296	0.372143
27	76	0	1.723408	-0.022506	1.406648
28	6	0	1.420667	-4.064326	-1.446144
29	1	0	2.290598	-3.618615	-0.959086
30	1	0	1.689305	-5.074432	-1.767565
31	1	0	1.183088	-3.471971	-2.334332
32	6	0	-1.010324	-4.673858	-1.145759
33	1	0	-0.829805	-5.696153	-1.486152
34	1	0	-1.842185	-4.685837	-0.438995
35	1	0	-1.303517	-4.071078	-2.009789

Sum of electronic and thermal Energies=				-1162.950881	
Sum of electronic and thermal Enthalpies=				-1162.949937	
Sum of electronic and thermal Free Energies=				-1163.018746	

Structural Parameters for the Non-alcohol Assisted Mechanism and The Hydrogenation of Acetone

Figure 2. Schematic drawing of the catalyst for reference proposes when referring to the structural parameters and APT charges listed in Table 2, Table 3 and Table 4.

Table 2. Selected bond distances for the calculated structures shown in Scheme 1.

Species	Selected Bond Lengths (Å)											
	Os-P1	Os-P2	Os-N1	Os-N2	Os-H1	Os-H2	Os-H3	H1-H2	N1-H1	O1-C2	O1-H2	C2-H1
A	2.24	2.27	1.98	2.19	n/a	n/a	1.61	n/a	n/a	n/a	n/a	n/a
B	2.25	2.29	2.13	2.20	1.80	1.81	1.64	0.85	2.42	n/a	n/a	n/a
BP1 N1	2.26	2.29	2.13	2.20	1.80	1.82	1.64	0.85	2.45	n/a	n/a	n/a
BNH2	2.26	2.29	2.12	2.19	1.79	1.81	1.64	0.85	2.58	n/a	n/a	n/a
BP1 P2	2.26	2.29	2.13	2.19	1.81	1.82	1.64	0.84	2.96	n/a	n/a	n/a
C*	2.25	2.26	2.19	2.19	1.83	1.81	1.66	1.02	1.42	n/a	n/a	n/a
D	2.24	2.24	2.20	2.20	2.68	1.72	1.72	2.54	1.01	n/a	n/a	n/a
E	2.23	2.24	2.20	2.20	2.72	1.72	1.72	2.63	1.02	1.22	2.00	2.90
F*	2.24	2.25	2.17	2.20	2.66	1.76	1.69	2.44	1.03	1.24	1.78	1.76
G	2.24	2.27	2.00	2.19	3.00	3.48	1.60	2.20	1.98	1.41	0.98	1.10

Table 3. Selected bond angles for the calculated structures shown in Scheme 1.

	Selected Bond Angles (°)		
Species	Os-N1-H4	H4-N1-C1	C1-N1-Os
A	125.4	112.1	119.9
B	112.0	108.2	109.5
B_{P1 N1}	112.5	108.2	109.7
B_{NH2}	113.3	108.2	110.0
B_{P1 P2}	112.5	108.2	109.6
C*	116.5	113.0	110.3
D	110.5	110.2	109.4
E	110.1	109.6	109.4
F*	113.0	110.0	110.0
G	124.0	111.4	118.9

Table 4. Selected bond angles for the calculated structures shown in Scheme 1.

	Selected APT Charges (ESU)								
Species	P1	P2	N1	N2	H1	H2	H3	O1	C2
A	1.1	1.1	-0.52	-0.25	n/a	n/a	-0.06	n/a	n/a
B	1.08	1.06	-0.54	-0.26	0.10	0.11	-0.08	n/a	n/a
B_{P1 N1}	1.07	1.06	-0.55	-0.26	0.12	0.09	-0.08	n/a	n/a
B_{NH2}	1.07	1.08	-0.56	-0.25	0.14	0.05	-0.08	n/a	n/a
B_{P1 P2}	1.08	1.08	-0.55	-0.26	0.15	0.05	-0.08	n/a	n/a
C*	1.10	1.11	-0.52	-0.27	0.46	-0.17	-0.11	n/a	n/a
D	1.15	1.15	-0.28	-0.28	0.14	-0.21	-0.21	n/a	n/a
E	1.12	1.14	-0.30	-0.26	0.22	-0.24	-0.20	-0.77	0.84
F*	1.10	1.12	-0.28	-0.27	0.21	-0.45	-0.22	-0.95	1.34
G	1.05	1.07	-0.57	-0.25	0.39	-0.08	-0.06	-0.77	0.51

Structural Parameters for iPrOH Assisted H₂ Splitting

Figure 3. Schematic drawing of the catalyst for reference proposes when referring to the structural parameters and APT charges listed in

Table 5. Selected bond lengths for the calculated structures shown in Scheme 1.

Selected Bond Lengths (Å)												
Species	Os-P1	Os-P2	Os-N1	Os-N2	Os-H1	Os-H2	Os-H3	H1-H2	N1-H1	O1-H1	O2-H5	N1-H5
H	2.25	2.29	2.14	2.19	1.82	1.80	1.64	0.84	2.47	2.42	1.02	1.66
J*	2.26	2.28	2.16	2.20	1.91	1.81	1.65	0.86	2.42	1.83	1.40	1.14
K	2.24	2.24	2.20	2.20	2.79	1.74	1.70	1.53	2.63	0.99	1.99	1.02

Table 6. Selected bond angles for the calculated structures shown in Scheme 1.

Selected Bond Angles (°)			
Species	Os-N1-H4	H4-N1-C1	C1-N1-Os
H	111.0	107.9	109.4
J*	115.0	110.2	110.0
K	109.8	109.8	109.0

Table 7. Selected APT charges for the calculated structures shown in Scheme 1.

Selected APT Charges (ESU)									
Species	P1	P2	N1	N2	H1	H2	H3	O1	C2
H	1.07	1.10	-0.62	-0.27	0.14	0.13	-0.07	-0.98	0.58
J*	1.05	1.07	-0.56	-0.27	0.40	-0.01	-0.10	-1.25	0.61
K	1.11	1.14	-0.32	-0.27	0.50	-0.28	-0.20	-0.97	0.23