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Acceptorless and Base-Free Dehydrogenation of Alcohols and Amines using Ruthenium-Hydride Complexes

Senthilkumar Muthaiah[b] and Soon Hyeok Hong[a,*]

[a] Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-747, Korea
Fax: (+82)-2-889-1568; phone: (+82)-2-880-6655; e-mail: soonhong@snu.ac.kr
[b] Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

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Abstract: An efficient, operatively simple, acceptorless, and base-free dehydrogenation of secondary alcohols and nitrogen-containing heterocyclic compounds was achieved by using readily available ruthenium hydride complexes as precatalysts. The complex $RuH_2(CO)(PPh_3)_3$ (**1**) and Shvo's complex (**2**) showed excellent activities for the dehydrogenation of secondary alcohols and nitrogen containing heterocycles. In addition to complexes **1** and **2**, the complex $RuH_2(PPh_3)_4$ (**3**) also showed moderate to excellent activity for the acceptorless dehydrogenation of nitrogen-containing heterocyclic compounds. Kinetic studies on the oxidation reaction of 1-phenylethanol using complex **1** were carried out in the presence and the absence of external triphenylphosphine (PPh_3). External addition of PPh_3 had a negative influence on the rate of the reaction, which suggested that dissociation of PPh_3 occurred during the course of the reaction. Hydrogen was evolved from the oxidation reaction of 1-phenylethanol by using 1 mol% of **1** (88%) and **2** (92%), which demonstrated the possible usage of the catalytic systems in hydrogen generation.

Keywords: alcohols; dehydrogenation; N-heterocycles; oxidation; ruthenium; Shvo's catalyst

Introduction

Oxidation reactions of alcohols[1] and amines[2] are fundamentally important in chemistry with wide applications. Traditional methods for the oxidation of alcohols involve stoichiometric amounts of oxidants such as hypochlorite,[3] chromium salts,[4] manganese salts,[5] oxalyl chloride,[6] and hypervalent iodines.[7] Several transition metal complexes, such as Ru,[8] Rh,[9] Ir[10] and Au[11] complexes, in the presence of stoichiometric amounts of oxidizing agents have been extensively used as catalysts in the oxidation reactions.[12] Examples of the oxidizing agents are peroxides, PhIO, *N*-methylmorpholine *N*-oxide, 2,6-dimethoxybenzoquinone and $K_2S_2O_8$. However, from both environmental and economic points of views, the use of stoichiometric amounts of oxidants is undesirable.

Significant efforts have been made to develop catalytic oxidations with environmentally friendly oxidants. Transition metal-catalyzed, acceptorless dehydrogenation reactions are one of the environmentally benign solutions for the oxidations, providing a possible platform for storage and transportation of H_2.[13] Recent experimental and theoretical studies showed that, similar to alcohols, nitrogen-containing heterocycles can also serve as the organic hydrides which can act as potential hydrogen storage systems.[14] The inclusion of nitrogen into the cyclic system facilitates the dehydrogenation process by decreasing the endothermicity of the reaction.[14]

Notwithstanding their potential applications in environmentally friendly oxidation and hydrogen storage, not so many catalytic systems have been developed for the acceptorless and oxidant- or base-free dehydrogenation of alcohols and nitrogen-containing heterocycles.[10,13] Among all the transition metal complexes employed in the dehydrogenation reactions, ruthenium complexes have played a vital role. However, most of the reported ruthenium catalytic systems for the dehydrogenation reactions of alcohols and amines used more than stoichiometric amounts of reagents such as hydrogen acceptors, bases, and/or oxidants, which are not atom-economical and environmentally benign. A number of ruthenium complexes in combination with oxidants, such as *t*-BuOOH,[8a] dioxygen,[15] iodosylbenzene,[16] and persulfate ions,[17] or hydrogen acceptors such as 1,4-benzoquinone[18] have

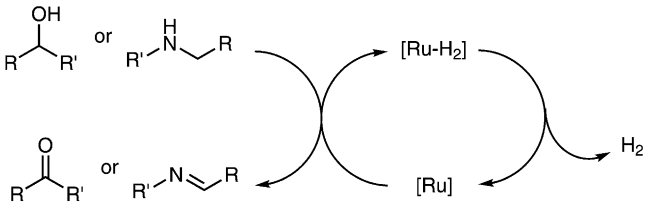
shown good to excellent activities for the dehydrogenation.

For example, the reported ruthenium-based catalytic systems that showed excellent activities without any hydrogen acceptors, but needed a promoter or a basic condition are $[Ru(OCOCF_3)(CO)(PPh_3)_2]$ with CF_3COOH as a promoter,[19] base-promoted ruthenium hydride-phosphine systems,[20] $RuCl_3$ hydrate/phosphine and $[RuCl_2(p\text{-cymene})]_2$/nitrogen-containing ligands in a basic medium,[21] Grubbs' catalyst and $[RuCl_2(p\text{-cymene})]_2/PPh_3$ system with LiOH,[22] and pincer diamine and diphosphane Ru complexes with a catalytic amount of KO-*t*-Bu.[8f]

Hydrogen acceptorless and base- or additive-free oxidations have been reported with rather specially designed catalytic systems such as heterogeneous Shvo-type ruthenium complex,[23] a recyclable Ru/AlO(OH) system,[24] dinuclear ruthenium complexes bearing dicarboxylate and phosphine ligands,[25] triazolidene ruthenium complexes,[26] and PNP- and PNN-type pincer ruthenium complexes.[27] In addition, Hartwig and co-workers have shown that some ruthenium complexes, including hydrido-phosphine, diphosphine-diamine, and Shvo's complex, are active for the dehydrogenation of 1,4-butanediol to γ-butyrolactone.[28]

During our study on Ru-catalyzed oxidative C–N bond formation reactions directly from alcohols and amines through hydrogen acceptor-free dehydrogenation of alcohols,[29] we became interested in alcohol or amine oxidation with simpler ruthenium precursors without using any hydrogen acceptor and/or a base. As dehydrogenation of alcohols can be facilitated by hydrogen elimination from dihydride intermediates at elevated temperatures and oxidative addition of hydroxy or amine N–H to a transition metal center can happen without any assistance of a base, we envisioned that hydrogen acceptorless and base-free oxidation of alcohol or amine could be realized with more readily available Ru hydride species (Scheme 1).

In this report, we investigated a series of readily available ruthenium hydride complexes for the acceptorless and oxidant-free dehydrogenation of secondary alcohols and nitrogen-containing cyclic systems under neutral reaction conditions. Several secondary alcohols have been oxidized to their corresponding ketones in moderate to excellent yields by using $RuH_2(CO)(PPh_3)_3$ (**1**) and Shvo's complex (**2**). Besides, the activities of complexes **1**, **2**, and $RuH_2(PPh_3)_4$ (**3**) were tested for the dehydrogenation of nitrogen-containing heterocyclic compounds. Furthermore, to gain more insight into the mechanism involving the dehydrogenation of alcohol using **1**, we carried out a series of kinetic studies in the presence of externally added PPh_3. The results supported a phosphine ligand dissociative mechanism.



Scheme 1. Basic principle of hydrogen acceptor- and base-free dehydrogenation of alcohol and amine.

Results and Discussion

Preliminary results on the oxidation of 1-phenylethanol (**7a**) to acetophenone (**8a**) using a variety of ruthenium hydride complexes such as $RuH_2(CO)(PPh_3)_3$ (**1**), Shvo's complex (**2**), $RuH_2(PPh_3)_4$ (**3**), $RuHCl(CO)(PPh_3)_3$ (**4**) and Ru(0) complexes such as $Ru_3(CO)_{12}$ (**5**) and Ru(cod)(cot) (**6**) are shown in Table 1. Complex **1** gave **8a** in a low yield of 33% under toluene reflux conditions (entry 1). The yield was dramatically increased when NaH was added as a base (entry 2). Matched with our hypothesis in Scheme 1, the corresponding ketone was produced in an excellent yield even in the absence of a base at an elevated temperature of 165 °C (entry 3). This result suggested that the oxidative addition of an O–H bond itself in a neutral condition, without generation of an alkoxide under a basic condition, requires higher temperature conditions. The catalytic activity was maintained with a lowered catalyst loading of 1 mol% (entry 5). However, further decreases in the catalyst loading resulted in diminished activities (entries 3 to 7). Then, we checked the activities of ruthenium-hydride complexes **2**–**4**. The results clearly indicated that all of the ruthenium-hydride complexes have the ability to oxidize the alcohol **7a** into ketone **8a** with moderate to excellent yields, even in the absence of any base, additive, or hydrogen acceptor. Among the complexes, **1** and **2** showed the best activities (entries 5 and 9). Ruthenium(0) complexes such as **5** and **6** showed much less activity compared to ruthenium hydride complexes (entries 17 and 18). Shvo's complex (**2**) showed the highest turnover number of 2600 when a 0.01 mol% catalyst loading used (entry 12).

Having these optimized conditions in hand, we then examined the scope of the reaction using complexes **1** and **2** under a gentle flow of argon to assist the removal of hydrogen generated during the reaction (Table 2). Various secondary alcohols were successfully oxidized to the corresponding ketones in moderate to excellent yields. Initially, oxidation reactions of a range of substituted 1-phenylethanols were tried. All of the derivatives of 1-phenylethanol tested gave their corresponding ketones in moderate to ex-

Table 1. Optimization of reaction conditions for dehydrogenation of 1-phenylethanol (**7a**).[a]

Entry	[Ru] (mol%)	Base	Solvent	Yield[b] of **8a** [%] (TON)
1	$RuH_2(CO)(PPh_3)_3$ **1** (5)	none	toluene	33
2	$RuH_2(CO)(PPh_3)_3$ (5)	NaH[c]	toluene	84
3	$RuH_2(CO)(PPh_3)_3$ (5)	none	mesitylene	98
4	$RuH_2(CO)(PPh_3)_3$ (2.5)	none	mesitylene	98
5	$RuH_2(CO)(PPh_3)_3$ (1)	none	mesitylene	98 (98)
6	$RuH_2(CO)(PPh_3)_3$ (0.1)	none	mesitylene	58 (580)
7	$RuH_2(CO)(PPh_3)_3$ (0.01)	none	mesitylene	0
8	Shvo's complex **2** (5)	none	mesitylene	96
9	Shvo's complex (1)	none	mesitylene	96 (96)
10	Shvo's complex (0.5)	none	mesitylene	85 (170)
11	Shvo's complex (0.1)	none	mesitylene	75 (750)
12	Shvo's complex (0.01)	none	mesitylene	26 (2600)
13	$RuH_2(PPh_3)_4$ **3** (5)	none	toluene	34
14	$RuH_2(PPh_3)_4$ (5)	NaH[c]	toluene	67
15	$RuH_2(PPh_3)_4$ (5)	none	mesitylene	49
16	$RuHCl(CO)(PPh_3)_3$ **4** (5)	none	mesitylene	95
17	$Ru_3(CO)_{12}$ **5** (1)	none	mesitylene	36
18	Ru(cod)(cot) **6** (1)	none	mesitylene	30

[a] [Ru] complex (x mol%), alcohol (1.0 equiv.), reflux (110 °C, toluene; 165 °C, mesitylene), 24 h.
[b] Determined by GC using dodecane as an internal standard, average of at least two runs.
[c] 10 mol% of NaH was used.

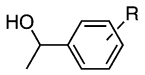
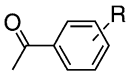
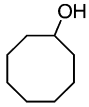
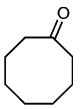
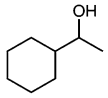
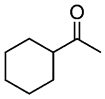
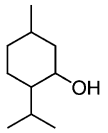
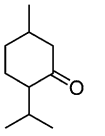
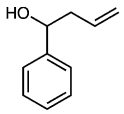
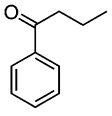
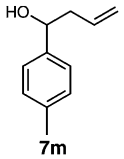
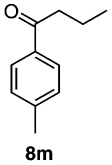
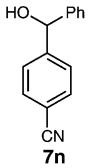
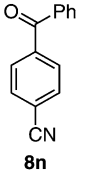
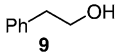
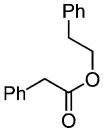
cellent yields (entries 1 to 8). Comparable yields were obtained when methoxy group was present either in the *meta*- or *para*-positions of the phenyl ring (entries 3 and 4). Functional groups such as ether (entry 4), halogen (entries 5 and 6), amide (entry 7), and amino groups (entry 8) can be tolerated in our catalytic systems. The presence of amide and amino groups did not have a significant influence on the activity of **2**, whereas considerably diminished yields of **8g** and **8h** were observed with **1** (entries 7 and 8). An aliphatic cyclic secondary alcohol such as cyclooctanol (**7i**) gave an excellent yield of cyclooctanone (**8i**) (entry 9). In the case of bulky secondary alcohols such as 1-cyclohexylethanol (**7j**) and menthol (**7k**), complex **2** showed better activity than complex **1**.

When olefinic secondary alcohols such as **7l** and **7m** were reacted, they gave the double bond reduced ketones, **8l** and **8m**, in excellent yields (entries 12 and 13). The oxidation of primary alcohol such as 2-phenylethanol (**9**) did not give the corresponding aldehyde, instead, it resulted in the formation of an ester **10** (entry 15). The formation of the ester from primary alcohols using ruthenium hydride complexes has been well reported previously.[30]

The results prompted us to measure the amount of hydrogen evolved out of the reaction. The hydrogen evolution was measured using a gas burette apparatus in the dehydrogenation reaction of **7a** using 1 mol% of precatalysts **1** and **2**.[31] Complexes **1** and **2** produced hydrogen with 88% and 92% yields, respectively. When a lowered catalyst loading of 0.1 mol% was used, complexes **1** and **2** gave 46% and 73% of H_2, respectively.

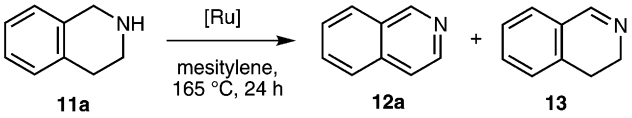
Encouraged by the above results, dehydrogenations of nitrogen-containing heterocycles were tested. Recent theoretical and experimental studies have shown that similar to alcohols, nitrogen-containing heterocycles can also act as potential hydrogen storage systems.[14a] As a beginning of this study, we tested ruthenium complexes **1**–**4** for the dehydrogenation of 1,2,3,4-tetrahydroisoquinoline (**11a**) under base- and oxidant-free reaction conditions (Table 3). When 1 mol% of **1** was used, both the fully and the partially dehydrogenated products isoquinoline (**12a**) and 3,4-dihydroisoquinoline (**13**) were formed in low yields (entry 1). Increase of the catalyst loading to 2.5 mol% resulted in **12a** as the major product in an improved yield of 53% (entry 2). When the catalyst loading was increased to 5 mol%, only the product **12a** was formed in 73% yield and there was no observation of **13** (entry 3). Other reported systems such as $Ru_2(OAc)_4Cl/O_2$,[8b] $Rh_2(cap)_4/t$-BuOOH,[9] and $RuCl_2(PPh_3)_3/PhIO$,[32] exclusively resulted in the formation of partially dehydrogenated product **13** with little or no formation of compound **12a**. A maximum yield of 65% of compound **12a** was reported while using $RuCl_2(PPh_3)_3$ as catalyst along with large excess of Bu^tOOH (5 equiv.) as an oxidant.[8a] Notably, our oxidant-free catalytic conditions produced **12a** as the major product. Consistent with the results of the alcohol dehydrogenations, an excellent yield of 99% was obtained when **2** was used (entry 5). Complexes **3** and

Table 2. Oxidation of alcohols using ruthenium-hydride complexes[a]

Entry	Substrate	Product	Yield [%][b] with catalyst 1	2
				
1	R = H (**7a**)	**8a**	98	96 (87)
2	R = 4-Me (**7b**)	**8b**	99	99 (88)
3	R = 4-OMe (**7c**)	**8c**	93	100 (94)
4	R = 3-OMe (**7d**)	**8d**	100	99 (91)
5	R = 3-Cl (**7e**)	**8e**	100	100 (92)
6	R = 4-Cl (**7f**)	**8f**	85	94 (88)
7	R = 3-NH(CO)CH_3 (**7g**)	**8g**	64	86 (73)
8	R = 4-NH_2 (**7h**)	**8h**	12	86 (77)
9	 **7i**	 **8i**	93	89 (84)
10	 **7j**	 **8j**	67	94 (91)
11	 **4k**	 **8k**	36[c]	81 (69)
12	 **7l**	 **8l**	100	98 (92)
13	 **7m**	 **8m**	83	100 (96)
14	 **7n**	 **8n**	45	58 (42)
15	 **9**	 **10**	77	98

[a] Ru complex (1 mol%), alcohol (1.0 equiv.), mesitylene, 165 °C, 24 h.
[b] Determined by GC using dodecane as the internal standard and average of at least two runs. Isolated yield in parenthesis.
[c] 36 h.

Table 3. Catalyst screening for the dehydrogenation of **9**.[a]



11a **12a** **13**

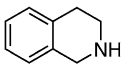
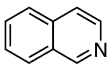
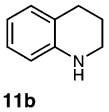
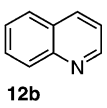
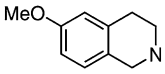
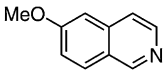
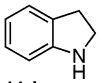
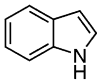
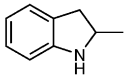
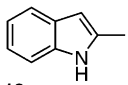
Entry	[Ru] (mol%)	Yield of **12a** [%][b]	Yield of **13** [%][b]
1	$RuH_2(CO)(PPh_3)_3$ **1** (1)	28	30
2	$RuH_2(CO)(PPh_3)_3$ (2.5)	53	5
3	$RuH_2(CO)(PPh_3)_3$ (5)	73	0
4	Shvo's complex **2** (1)	82	0
5	Shvo's complex (2.5)	99	0
6	$RuH_2(PPh_3)_4$ **3** (5)	78	0
7	$RuHCl(CO)(PPh_3)_3$ **4** (5)	64	3

[a] Ru complex (x mol%), amine (1.0 equiv), mesitylene, 165 °C, 24 h.[b] Determined by GC using dodecane as an internal standard and average of at least two runs.

4 showed moderate activities with major production of compound **12a** (entries 6 and 7).

After optimization of the reaction conditions, we extended the substrate scope using complexes **1**, **2** and **3** (Table 4). Compared to **11a**, 1,2,3,4-tetrahydroquinoline (**11b**) required a longer reaction time. An excellent yield (98%) of **12b** was obtained in 48 h

Table 4. Dehydrogenation of nitrogen-containing heterocyclic compounds.[a]

Entry	Substrate	Product	Yield[b] with catalyst 1	2	3
1	 **11a**	 **12a**	73	99 (91)	78
2	 **11b**	 **12b**	45[c]	98[c] (93)[c]	32[c]
3	 **11c**	 **12c**	87	100 (96)	74
4	 **11d**	 **12d**	95	98 (93)	89
5	 **11e**	 **12e**	97	100 (96)	73

[a] Ru complex (5 mol% of [Ru], that is, 2.5 mol% for **2**), amine (1.0 equiv.), mesitylene, 165 °C, 24 h unless otherwise noted.
[b] Determined by GC using dodecane as an internal standard and average of at least two runs. Isolated yield in parenthesis.
[c] 48 h

when **2** was used. Other ruthenium complexes **1** and **3** gave **12b** in moderate yields after 48 h (entry 2). 6-Methoxy-1,2,3,4-tetrahydroisoquinoline **11c** gave good to excellent yields of the product **12c** (entry 3). Dehydrogenations of indolines were highly efficient with all three ruthenium complexes (entries 4 and 5).

Morton and Cole-Hamilton reported an $RuN_2H_2(PPh_3)_3$-catalyzed dehydrogenation of alcohols in a basic medium.[20] They proposed a mechanism, in which the first step involves the displacement of dinitrogen ligand by an alkoxide moiety. Then, the resulting alkoxide complex undergoes β-hydride transfer to form the oxidation product, aldehyde or ketone. Further, an anionic ruthenium trihydride complex $[RuH_3(PPh_3)_3]^-$ was suggested to be the resting state of the catalyst. It was argued that release of dihydrogen would be rate-limiting and the three PPh_3 ligands could remain coordinated to the metal center during the process.[20a] However, Shinoda and co-workers showed that externally added phosphines in the reaction mixture retard the reaction, which indicated that the reaction mechanism involves PPh_3 ligand dissociation.[33] A recent theoretical study by Bolm and coworkers suggested that the dehydrogenation reaction of methanol using $[RuN_2H_2(PPh_3)_3]$ complex preferentially proceeds through dissociation of one of the phosphine ligands.[34] The mechanism also involves intermolecular proton transfer from methanol to the catalyst followed by the release of dihydrogen. The rate-limiting β-hydride elimination from the resulting methoxide species was proposed to regenerate the resting state of the catalyst and complete the catalytic cycle.

As the working mechanism of Shvo's catalyst's for alcohol dehydrogenation has been well studied,[35] we were keen to study the mechanism involved in $RuH_2(CO)(PPh_3)_3$ (**1**)-catalyzed oxidation of 1-phenylethanol (**7**). To investigate whether hydrogen, CO, or PPh_3 dissociates to generate an active catalytic species, we have carried out a series of kinetic studies with varied externally added PPh_3 concentrations. The kinetic studies were performed using 0, 5, 7.5 and 10 equiv. of external PPh_3 with respect to 0.00545 M of **1**. When the reciprocal of the rate constant was plotted as a function of concentration of added PPh_3, a linear dependence was observed (Figure 1). The rate dependence on $[PPh_3]$ is in good agreement with the other previous reports,[33] suggesting that the mechanism involves the phosphine ligand dissociative pathway similarly to Shinoda's[33] and Bolm's[34] studies.

In addition, through NMR spectroscopic investigation on the oxidation of 1-phenylethanol in mesitylene-d_{12}, we found that free PPh_3 was observed in ^{31}P NMR spectra within 5 min without any significant production of the oxidation product **8a**. Based on our experimental evidence and the literature reports, we

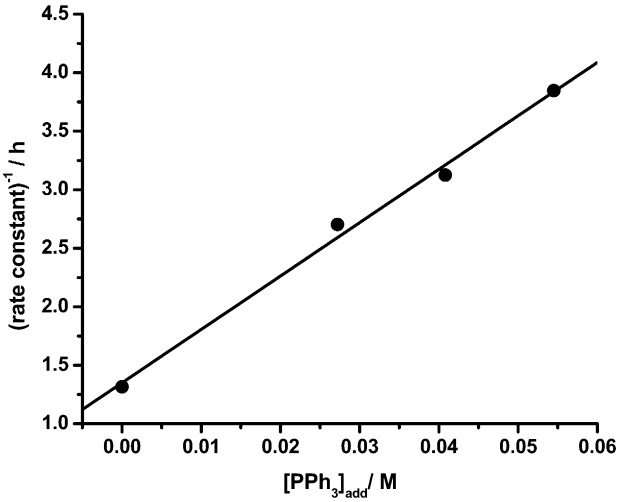
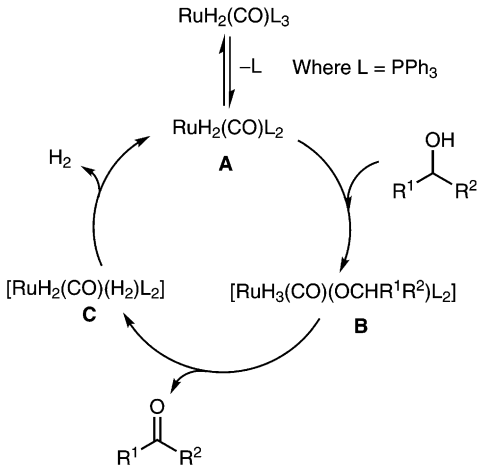


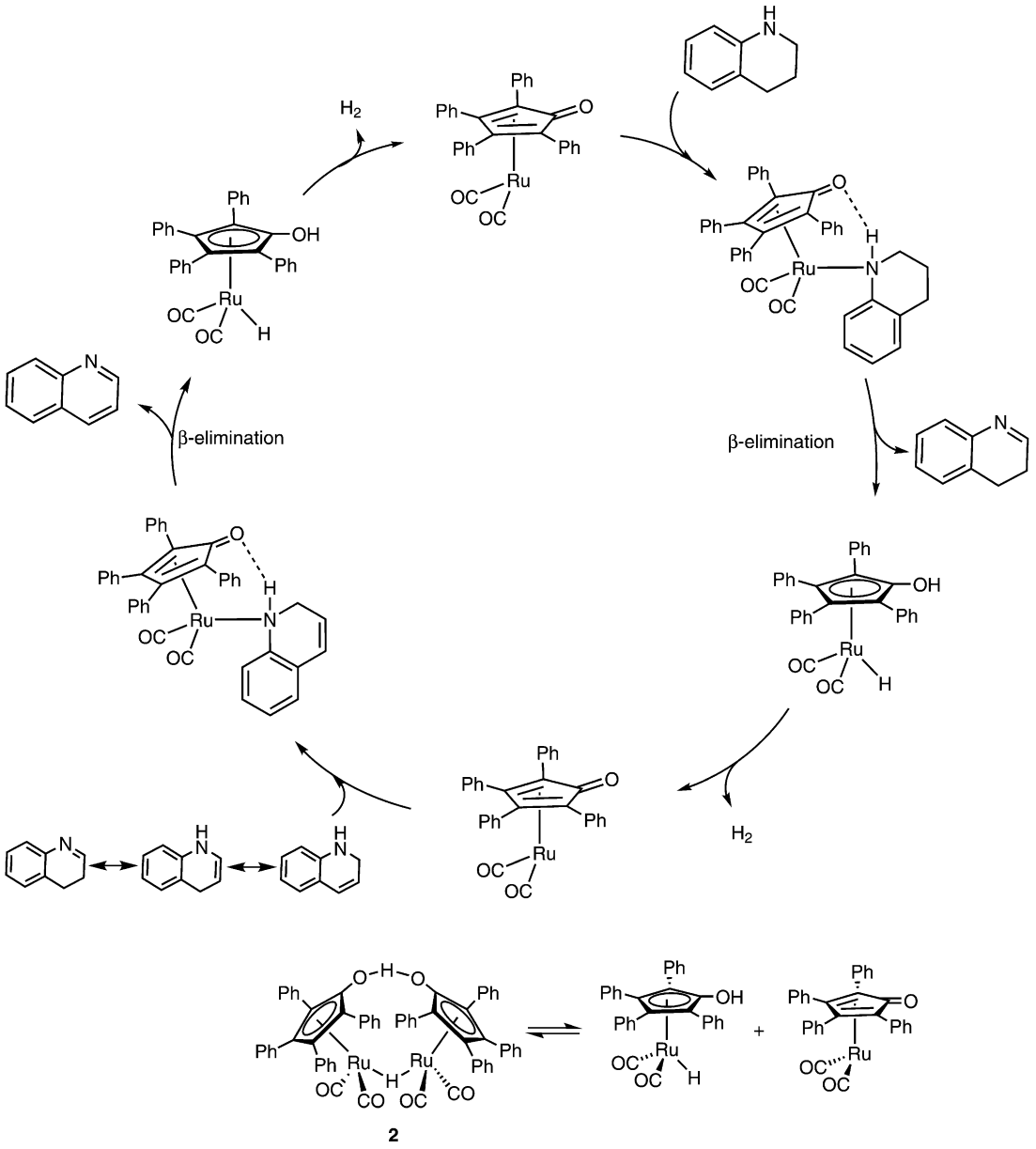
Figure 1. Effect of concentration of externally added PPh_3 on the rate of dehydrogenation of 1-phenylethanol

proposed a mechanism involving a ligand dissociative pathway (Scheme 2). The first step can be the dissociation of one of the phosphine ligands coordinated to the ruthenium to give a coordinatively unsaturated complex **A**. Complex **A** in turn can react with an alcohol to form ruthenium-alkoxide-trihydride complex **B**, which further undergoes β-hydride transfer followed by reductive elimination to give compound **C** and the product. Release of dihydrogen from complex **C** will reproduce the unsaturated complex **A** and complete the catalytic cycle.

A proposed mechanism for the N-heterocycle dehydrogenation by **2**, based on the reports on Shvo's complex-catalyzed amine dehydrogenation[8c] and Wang's mechanistic proposal on the dehydrogenation of N-heterocycles,[36] is illustrated in Scheme 3.



Scheme 2. Proposed catalytic cycle for the dehydrogenation of alcohols using $RuH_2(CO)(PPh_3)_3$.



Scheme 3. Proposed catalytic cycle for the dehydrogenation of an N-heterocycle using Shvo's complex.

Conclusions

In summary, we have reported an acceptorless, base- and oxidant-free dehydrogenation of secondary alcohols and nitrogen-containing heterocyclic compounds using commercially available $RuH_2(CO)(PPh_3)_3$, Shvo's complex, and $RuH_2(PPh_3)_4$, under neutral reaction conditions. Among the ruthenium-hydride complexes tested, Shvo's complex showed the best activity for the oxidation of both secondary alcohols and nitrogen-containing heterocyclic compounds. Notably, the dehydrogenation of 1,2,3,4-tetrahydroisoquinoline exclusively resulted in the formation of the completely dehydrogenated product, isoquinoline, which shows the stronger oxidizing ability of our catalytic systems in comparison with other reported systems. Hydrogen evolution measurements showed that the reported catalytic processes could provide a possible platform for the storage and transformation of H_2. The kinetic and NMR studies suggested that the mechanism involves the PPh_3 ligand dissociation pathway when $RuH_2(CO)(PPh_3)_3$ was used as a precatalyst.

Experimental Section

General Considerations

All reactions were carried out using standard Schlenk technique under inert argon atmosphere. Toluene and THF

were dried over a solvent purification system.[37] Anhydrous mesitylene was purchased from Aldrich and used without further purification. GC analyses were carried out using dodecane as an internal standard. Shvo's complex (**2**) was purchased from Strem and used without further purification. $RuH_2(CO)(PPh_3)_3$ (**1**),[38] $RuH_2(PPh_3)_4$ (**3**),[39] and $RuHCl(CO)(PPh_3)_3$ (**4**)[38] were prepared according to the reported procedures.

General Procedure for Dehydrogenation

Ruthenium complex (1 mol% for alcohol oxidation and 5 mol% for amine oxidation) and mesitylene (0.6 mL) were placed in an oven-dried Schlenk tube inside the glove box. The Schlenk tube was taken out and starting material (1.0 equiv.) was added under an argon atmosphere. The reaction mixture was heated at 165 °C for 24 h in an oil bath with a cooling reflux condenser under a gentle flow of argon to facilitate removal of hydrogen. After completion of the reaction, the flask was cooled to room temperature, and dodecane (1.0 equiv.) was added as an internal standard. The reaction mixture was filtered through neutral alumina using dichloromethane as the solvent and injected into GC for analysis. GC yields were measured and calculated considering the detector response factor of the product *versus* dodecane. For isolation of the products, the flask was cooled to room temperature after completion of the reaction. All volatiles were removed under vacuum, and the residue was purified by silica gel flash chromatography to afford the pure dehydrogenated product. All the dehydrogenated products were identified by spectral comparison with literature data.

Acetophenone (8a):[40] Purified by silica gel column chromatography (hexane:EA 9:1) to give a colourless oil; isolated yield: 87% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.6$ (s, 3H), 7.2–7.5 (m, 3H), 7.9 (m, 2H).

1-*p*-Tolylethanone (8b):[40] Purified by silica gel column chromatography (hexane:EA 9:1) to give a colourless oil; isolated yield: 88% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.39$ (s, 3H), 2.58 (s, 3H), 7.25 (m, 2H), 7.84 (m, 2H).

1-(4-Methoxyphenyl)ethanone (8c):[41] Purified by silica gel column chromatography (hexane:EA 4:1) to give a colourless oil; isolated yield: 94% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.54$ (s, 3H), 3.86 (s, 3H), 6.91–6.93 (m, 2H), 7.91–7.94 (m, 2H).

1-(3-Methoxyphenyl)ethanone (8d):[42] Purified by silica gel column chromatography (hexane:EA 4:1) to give a colourless oil; isolated yield: 91% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.5$ (s, 3H), 3.8 (s, 3H), 7.10 −7.12 (m, 1H), 7.35–7.38 (m, 1H), 7.48–7.54 (m, 2H).

1-(3-Chlorophenyl)ethanone (8e):[43] Purified by silica gel column chromatography (hexane:EA 7:3) to give a colourless oil; isolated yield: 92% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.54$ (s, 3H), 7.25–7.41 (m, 1H), 7.51–7.54 (m, 1H), 7.80–7.84 (m, 1H), 7.91–7.92 (d, 1H).

1-(4-Chlorophenyl)ethanone (8f):[40] Purified by silica gel column chromatography (hexane:EA 7:3) to give a colourless oil; isolated yield: 88% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.57$ (s, 3H), 7.42 (d, 2H), 7.88 (d, 2H).

***N*-(3-Acetylphenyl)acetamide (8g):**[44] Purified by silica gel column chromatography (hexane:EA 3:2) to give a off white solid; isolated yield: 73% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.21$ (s, 3H), 2.59 (s, 3H), 7.38–7.42 (m, 1H), 7.65–7.67 (m, 1H), 7.92–7.94 (m, 1H), 8.01 (s, 1H), 8.07 (bs, 1H).

1-(4-Aminophenyl)ethanone (8h):[45] Purified by silica gel column chromatography (hexane:EA 3:2) to give a white solid; isolated yield: 77% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.48$ (s, 3H), 4.09 (bs, 2H), 6.61 (m, 2H), 7.77 (m, 2H).

Cyclooctanone (8i):[46] Purified by silica gel column chromatography (hexane:EA 9:1) to give a colourless oil; isolated yield: 84% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.31$–1.37 (m, 2H), 1.48–1.55 (m, 4H), 1.81–1.88 (m, 4H), 2.36–2.40 (m, 4H).

1-Cyclohexylethanone (8j):[47] Purified by silica gel column chromatography (hexane:EA 9:1) to give a colourless oil; isolated yield: 91% (using complex **2**).^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.16$–1.35 (m, 5H), 1.64–1.86 (m, 5H), 2.10 (s, 3H), 2.30–2.32 (m, 1H).

Menthone (8k):[48] Purified by silica gel column chromatography (hexane:ether 1:1) to give a white solid; isolated yield: 69% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.85$ (d, 3H), 0.77 (d, 3H), 1.01 (d, 3H), 1.19–1.30 (m, 2H), 1.78–2.26 (m, 5H), 2.30–2.31 (m, 1H)

1-Phenylbutan-1-one (8l):[42] Purified by silica gel column chromatography (hexane:EA 4:1) to give a pale yellow liquid; isolated yield: 92% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.00$ (t, 3H), 1.74- 1.80 (m, 2H), 2.95 (t, 2H), 7.42–7.54 (m, 3H), 7.95 (m, 2H).

1-(4-Methylphenyl)butan-1-one (8m):[49] Purified by silica gel column chromatography (hexane:EA 4:1) to give a pale yellow liquid; isolated yield: 96% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.53$ (t, 3H), 1.30 (m, 2H), 1.93 (s, 3H), 2.45 (t, 2H), 6.7–6.79 (d, 2H), 7.39 (m, 2H).

4-Benzoylbenzonitrile (8n):[50] Purified by silica gel column chromatography (CH_2Cl_2:hexane 1:1) to give a white solid; isolated yield: 42% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.48$–7.52 (m, 2H), 7.62–7.76 (m, 1H), 7.77- 7.82 (m, 4H), 7.82–7.88 (m, 2H).

Isoquinoline (12a):[51] Purified by silica gel column chromatography (hexane:EA 7:3) to give a yellow liquid; isolated yield: 91% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.58$–7.70 (m, 3H), 7.80–7.82 (m, 1H), 7.95–7.97 (m, 1H), 8.51 (s, 1H), 9.24 (s, 1H).

Quinoline (12b):[51] Purified by silica gel column chromatography (hexane:EA 4:1) to give a pale yellow liquid; isolated yield: 93% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.36$–7.40 (m, 1H), 7.51–7.56 (m, 1H), 7.68–7.73 (m, 1H), 7.79–7.82 (m, 1H), 8.09–8.16 (m, 2H), 8.91(s, 1H).

6-Methoxyisoquinoline (12c):[52] Purified by silica gel column chromatography (hexane:EA 3:2) to give a yellow oil, isolated yield: 96% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.91$ (s, 3H), 7.09 (d, 1H), 7.33–7.38 (m, 2H), 8.00–8.06 (m, 2H), 8.74 (d, 1H).

Indole (12d):[53] Purified by silica gel column chromatography (hexane:EA 3:2) to give a white solid; isolated yield: 93% (using complex **2**). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 6.59 (s, 1H), 7.15–7.25 (m, 3H), 7.38–7.40 (m, 1H), 7.68–7.70 (m, 1H), 8.05 (bs, 1H).

2-Methylindole (12e):[53] Purified by silica gel column chromatography (hexane:EA 3:2) to give a white solid. Isolated yield: 96% (using complex **2**). ^{1}H NMR (400 MHz,

$CDCl_3$): $\delta = 2.43$ (s, 3H), 6.22 (s, 1H), 7.05–7.13 (m, 2H), 7.24–7.28 (m, 1H), 7.51–7.53 (m, 1H), 7.79 (bs, 1H).

Gas Burette Measurements

The volume of H_2 was quantitatively measured using a gas burette as reported in the literature.[31] In a typical procedure, $RuH_2(CO)(PPh_3)_3$ or Shvo's complex (0.01, 0.1 and 1 mol%) was placed in a Schlenk flask fitted with a side arm. To the flask, 1-phenylethanol (0.1 mL, 0.8 mmol) in mesitylene (1 mL) was added under an argon atmosphere. The Schlenk flask was connected to the gas burette *via* tubing and was heated in a preheated oil bath (165 °C). After a few seconds the side arm was opened up to the burette, and the reaction was continued for 24 h before taking the measurement of the increased volume.

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