

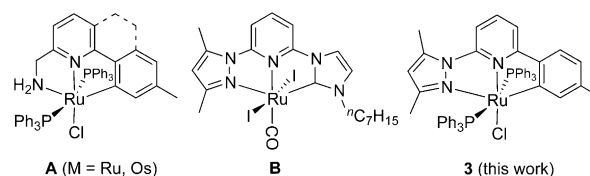
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A Versatile Ruthenium(II)–NNC Complex Catalyst for Transfer Hydrogenation of Ketones and Oppenauer-Type Oxidation of Alcohols

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Pyridyl-based ligands have been utilized as potential frameworks for useful organometallic materials and active complex catalysts.^[1] Pincer complexes of nonphosphorus tridentate NNN ligands, such as Pybox,^[2] 2,6-bis-(imino)pyridines,^[3] terpyridines,^[4] and other symmetrical polydentate ligands,^[5] have recently become more attractive targets due to their tunable properties and powerful applications.^[6,7] Although symmetrical ligands have been used to construct diverse transition-metal complexes, catalyst complexes containing unsymmetrical polydentate ligands usually exhibit unexpectedly high catalytic activity due to the precise control of their electronic and geometric properties.^[8–10] Thus, unsymmetrical polydentate ligands are highly desirable for complex catalyst design and functional materials fabrication.

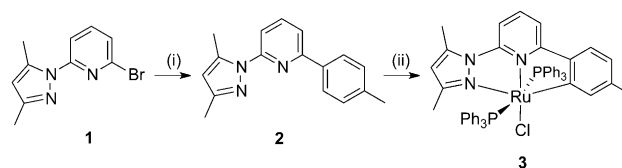
The transfer hydrogenation of ketones and Oppenauer-type dehydrogenative oxidation of alcohols have been extensively studied^[11] and have become reliable synthetic protocols beyond conventional reduction and oxidation reactions.^[12] Ruthenium(II) *N*-tosylethylenediamine complexes developed by Noyori and co-workers have been proven to be very efficient catalysts for asymmetric transfer hydrogenation of ketones.^[13] Cyclometalated complexes containing unsymmetrical NNC ligands have generally been utilized as phosphorescent materials in organic light-emitting devices and chemosensors;^[14] only a few examples have been applied as catalysts. Baratta et al. have documented the use of highly active ruthenium(II) NNC-complex catalysts (type **A**), with an NH₂ group as the accelerating functionality in 2-(aminomethyl)pyridine (ampy) ligands, for the transfer hydrogenation of ketones.^[10, 15] However, Ru^{II} complexes (type **B**) that contain a pyridyl-based pyrazolyl-*N*-heterocyclic carbene (NHC) ligand only exhibited a poor catalytic activity for the same reactions (final turnover frequency



(TOF) = 125 h⁻¹).^[9c] The NHC ligand has been known to be a strong σ -donor ligand, which may render transition-metal complexes containing this ligand less labile during a catalytic cycle.

During the ongoing investigation into transition-metal-complex catalysts, we envisioned that by using a carbanion to replace the NHC coordinating arm in the ligand, the resultant Ru^{II} complex containing an unsymmetrical NNC ligand may exhibit decent catalytic activity. Herein, we report a refined NNC-ligand-based Ru^{II}-complex catalyst for the transfer hydrogenation of ketones and the Oppenauer-type oxidation of alcohols.

Compound **2** was readily prepared in 86% yield by a palladium-catalyzed Suzuki coupling of **1** with *para*-tolylboronic acid. In the presence of triethylamine, Ru^{II} complex **3** was obtained from the reaction of **2** and an equimolar amount of [Ru(PPh₃)₃Cl₂] heated at reflux in 2-propanol in 65% yield (Scheme 1). Recrystallization of **3** from toluene/*n*-hexane



provided air-stable red-brown crystals. NMR spectroscopic analysis of **3** in solution supported the predicted structure. The ³¹P{¹H} NMR spectrum revealed a singlet at δ = 26.4 ppm, suggesting that two identical PPh₃ ligands were positioned *trans* to each other to reduce steric hindrance around the metal center. The molecular structure of **3** was further confirmed by X-ray crystallographic determination (Figure 1). In the solid state, complex **3** exhibits a neutral molecular structure with a nearly planar tridentate NNC ligand, which is generated from the deprotonation of **2**; the

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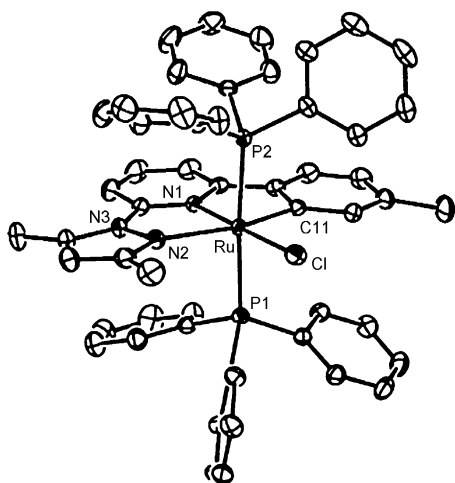


Figure 1. The molecular structure of complex **3**.

ruthenium atom is surrounded by two PPh₃ ligands, pyridyl and pyrazolyl nitrogen donor atoms, and one carbon atom in a distorted bipyrimidal environment. The Ru–C bond length is 2.034 Å, which is similar to that in Baratta and co-workers' Ru^{II} complex **A** (2.057 Å),^[10c] indicating the formation of a Ru–C σ bond. The bond lengths of Ru–N1 and Ru–N2 are 1.991 and 2.181 Å, respectively, which are longer than those (1.955 and 2.078 Å) in the ruthenium(II) complex that contains a symmetrical 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine ligand.^[16] This can presumably be attributed to the presence of two bulky PPh₃ ligands in complex **3**, which result in a labile molecular structure and thus lead to a higher catalytic activity for the transfer hydrogenation of ketones.

By using complex **3** as the catalyst (0.1 mol%), the transfer hydrogenation of ketones was carried out in 2-propanol at reflux in the presence of *i*PrOK (2 mol%) under a nitrogen atmosphere (Table 1). This catalytic system was applied to a variety of ketone substrates, including substituted aceto-

Table 1. Transfer hydrogenation of ketones catalyzed by complex **3**.^[a]

$$\text{R}^1-\text{C}(=\text{O})-\text{R}^2 + \text{OH} \xrightarrow[\textit{iPrOK}]{\mathbf{3} (0.1 \text{ mol } \%)} \text{R}^1-\text{C}(\text{OH})-\text{R}^2 + \text{O} \quad (1)$$

Entry	Ketone	Time [min]	Yield ^[b] [%]	Final TOF [h ⁻¹]	Entry	Ketone	Time [min]	Yield ^[b] [%]	Final TOF [h ⁻¹]
1		1	98	58 800	11		2/3	97	87 300
2		1	99	59 400	12		2	97	29 100
3		2	98	29 400	13		1/3	98	176 400
4		60	95	950	14		1	99	59 400
5		1	99	59 400	15		1	97	58 200
6		2	97	29 100	16		2	98	29 400
7		2/3	99	89 100	17		90	95	633
8		1	99	59 400	18		1	98	58 800
9		1/3	99	178 200	19		1	100	60 000
10		1/3	97	174 600	20		1/3	99	178 200

[a] Conditions: ketone (2.0 mmol, 0.1 M in 20 mL *i*PrOH); catalyst **3** (0.1 mol%); ketone/*i*PrOK/**3** = 1000:20:1; N₂ (0.1 MPa), 82 °C. [b] Determined by GC analysis.

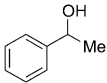
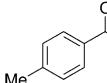
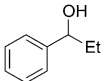
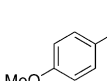
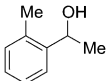
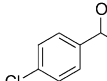
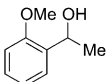
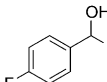
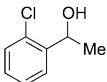
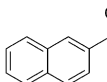
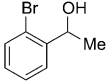
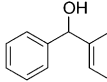
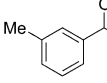
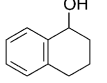
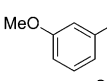
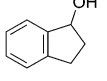
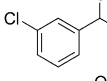
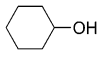
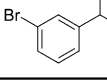
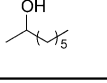
phenones and aliphatic cyclic and acyclic ketones, and was able to exclusively reduce ketones to their corresponding alcohols. In most cases, the ketone substrates reached >98% conversion within 1 min, with final TOF values of up to 178200 h⁻¹ (Table 1, entries 9 and 20). Electron-withdrawing substituents on the aryl rings of acetophenones usually accelerated the reaction, whereas the *ortho* substituents showed a steric effect that reduced the reaction rate (Table 1, entries 3–6). Compared with the catalytic activity of complex **B** and the catalyst containing a symmetrical NNN ligand [i.e., [RuCl₂(PPh₃)L] (L=2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine; final TOF=5940 h⁻¹)] under similar conditions,^[16] complex **3**, which is supported by the unsymmetrical NNC ligand, exhibited a remarkably high catalytic activity. It should be noted that the corresponding Ru^{II} complex containing the 2,6-bis(4-tolyl)pyridine ligand could not be successfully prepared for comparison. The enhancement in the catalytic activity of **3** is presumably due to the unsymmetrical environment around the metal center, which sug-

gests that the combined electronic and steric effects of the two different coordinating donor arms at the 2,6 positions of the pyridyl backbone are crucial for the complexes to exhibit a high catalytic activity.

The Oppenauer-type oxidation of alcohols has been widely used to synthesize carbonyl compounds in the absence of stoichiometric amounts of oxidants.^[17] In a fashion similar to the transfer hydrogenation of ketones, the dehydrogenative oxidation of secondary alcohols into ketones was performed (Table 2). By using complex **3** (0.5 mol%) as the catalyst and *t*BuOK (10 mol%) as the base for the reaction in acetone at reflux, secondary alcohols were exclusively oxidized to their corresponding ketones over a period of 1 min to 3 h. For most of the alcohol substrates, >97% conversion was obtained within 1–20 min with final TOF values of up to 11880 h⁻¹ (Table 2, entry 15), which represents one of the best catalytic systems for this type of reaction to date.^[17] Aliphatic alcohols were also oxidized to the corresponding ketones by using a higher catalyst loading over a

Table 2. Oxidation of alcohols catalyzed by complex **3**.^[a]

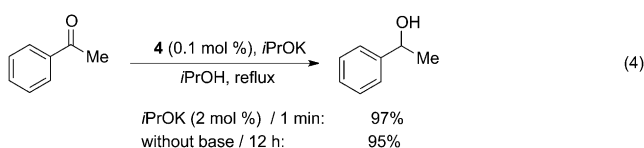
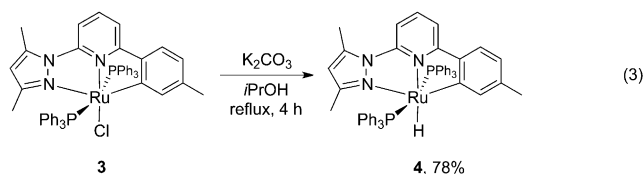
$$\text{R}^1\text{CH(OH)R}^2 + \text{O} \xrightarrow[\text{tBuOK}]{\text{3 (0.5 mol\%)}} \text{R}^1\text{C(O)R}^2 + \text{OH} \quad (2)$$

Entry	Alcohol	Time [min]	Yield ^[b] [%]	Final TOF [h ⁻¹]	Entry	Alcohol	Time [min]	Yield ^[b] [%]	Final TOF [h ⁻¹]
1		5	99	2376	11		10	99	1188
2		10	98	1176	12		10	98	1176
3		5	98	2352	13		10	97	582 ^[f]
4		5	99	594 ^[c]	14		20	98	588
5		120	97	9.7 ^[d]	15		1	99	11880
6		180	94	6.3 ^[d]	16		10	98	1176
7		5	98	2352	17		5	98	588 ^[e]
8		10	85	1020 ^[e]	18		3	100	4000
9		20	97	582	19		40	97	15 ^[g]
10		10	98	588 ^[f]	20		60	98	4.9 ^[h]

[a] Conditions: alcohol (2.0 mmol, 0.2 M in 10 mL acetone); catalyst **3** (0.5 mol%); alcohol/*t*BuOK/**3**=200:20:1; N₂ (0.1 MPa), 56 °C. [b] Determined by GC analysis. [c] 2 mol% catalyst was used. [d] 5 mol% catalyst was used. [e] Determined by ¹H NMR analysis. [f] 1 mol% catalyst was used. [g] 10 mol% catalyst was used. [h] 20 mol% catalyst was used.

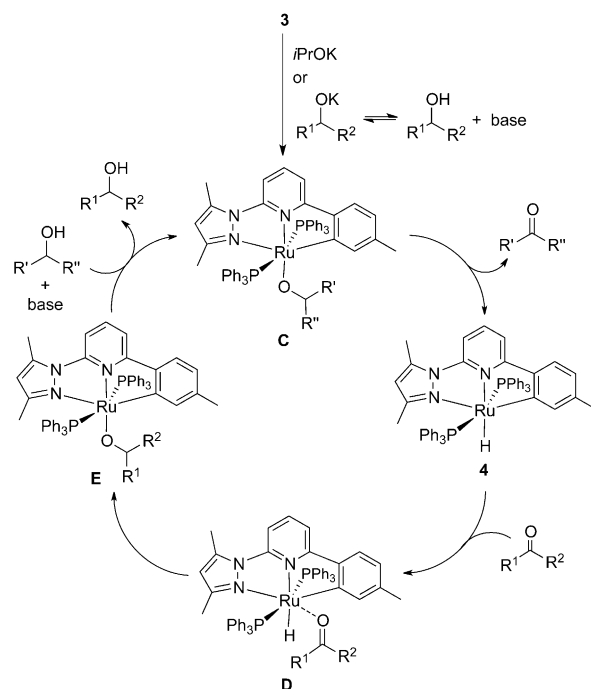
longer period (Table 2, entries 19 and 20). The *ortho* substituents on the aryl ring of the substrates had a negative effect on the reaction as a result of the increased steric hindrance (Table 2, entries 5 and 6).

An in situ generated Ru–H complex may act as the catalytically active species in the transfer hydrogenation of ketones.^[9a,15e,18] To verify this, complex **3** was treated with K₂CO₃ in 2-propanol at reflux to provide the Ru–H complex **4** in 78% yield [Eq. 3]. The ¹H NMR spectrum of **4** in solution revealed a triplet at $\delta = -8.57$ ppm, suggesting the presence of a Ru–H functionality in the complex. The ³¹P{¹H} NMR signal was a doublet at $\delta = 52.4$ ppm due to the P–H coupling interaction. Recently, we have successfully prepared and structurally characterized by X-ray crystallography the complex [RuCl(H)(NNN)(PPh₃)₂], which contains *trans*-PPh₃ ligands.^[9a] The crystal structure showed spectral features similar to those of **3**, thus complex **4** was structurally assigned as an analogue of **3**.



It was also observed that complex **3** did not result in the transfer hydrogenation of acetophenone in the absence of a base. Under the optimal conditions for the transfer hydrogenation of ketones (Table 1), Ru–H complex **4** exhibited a catalytic activity similar to that of complex **3** [Eq. 4 and Table 1, entry 1], providing a 97% yield of the desired product within 1 min when using *i*PrOK (2 mol%) as the base. However, without the use of a base, complex **4** only inefficiently promoted the reduction of acetophenone, providing a yield of 95% over a period of 12 h [Eq. 4]. These results suggest that both the Ru–H species and a suitable base are involved in the catalytic cycle.

A plausible inner-sphere mechanism is proposed in Scheme 2 to demonstrate that the Ru–H complex **4** is the catalytically active species^[19] for both the transfer hydrogenation and dehydrogenative oxidation pathways.^[20] The transfer hydrogenation pathway utilizes 2-propanol as both the solvent and hydrogen donor, whereas the oxidation pathway uses acetone as the solvent and hydrogen acceptor. Both of the pathways involve four steps: 1) under basic conditions, complex **3** initially forms Ru^{II}-alkoxide **C**, which undergoes β -H elimination to afford Ru–H intermediate **4**; 2) coordination of a ketone substrate (or acetone) to **4** generates species **D**; 3) insertion of the coordinated ketone car-



Scheme 2. Proposed mechanism for the transfer hydrogenation and dehydrogenative oxidation pathways.

bonyl into the Ru–H bond forms Ru^{II}-alkoxide **E**; and 4) base-mediated alcohol metathesis with **E** regenerates species **C** and completes the catalytic cycle. It is reasonable to propose that the exchange of the alkoxide product with another alcohol can be facilitated under basic conditions, which may provide an explanation for the inferior catalytic activity of **4** in the absence of a base [Eq. 4].

In conclusion, a versatile ruthenium(II) complex containing an unsymmetrical NNC ligand was synthesized and has exhibited highly catalytic activity for both transfer hydrogenation of ketones and Oppenauer-type oxidation of alcohols. The reversible redox reaction can easily be switched by changing the solvent from 2-propanol to acetone. The unsymmetrical environment around the complex metal center is crucial to the excellent catalytic activity of the complex catalyst, and the Ru–H species that is generated in situ is presumably the catalytically active intermediate.

Experimental Section

General procedure for the catalytic transfer hydrogenation of ketones:

The catalyst solution was prepared by dissolving complex **3** (18.5 mg, 0.02 mmol) in 2-propanol (20.0 mL). Under a nitrogen atmosphere, a mixture of a ketone (2.0 mmol), the catalyst solution (2.0 mL, 0.002 mmol), and 2-propanol (17.6 mL) was stirred at 82 °C for 10 min. Then, a solution of *i*PrOK (0.1 M, 0.04 mmol) in 2-propanol (0.4 mL) was introduced to initiate the reaction. At the stated time, 0.1 mL of the reaction mixture was sampled and immediately diluted with pre-cooled (0 °C) 2-propanol (0.5 mL) for GC analysis. After the reaction was complete, the reaction mixture was condensed under reduced pressure and subjected to purification by silica gel flash column chromatography to afford the

corresponding alcohol product, which was identified by comparison with the ¹H NMR spectrum and GC analysis of an authentic sample.

Acknowledgements

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Keywords: homogeneous catalysis • ketones • NNC ligands • ruthenium • transfer hydrogenation

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