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Oxo-Tethered Ruthenium(II) Complex as a Bifunctional Catalyst for Asymmetric Transfer Hydrogenation and H₂ HydrogenationTaichiro Touge,[†] Tomohiko Hakamata,[†] Hideki Nara,[†] Tohru Kobayashi,[†] Noboru Sayo,[†] Takao Saito,[†] Yoshihito Kayaki,[‡] and Takao Ikariya^{*,‡}[†]Corporate Research & Development Division, Takasago International Corporation, 4-11, Nishiyawata 1-chome, Hiratsuka City, Kanagawa 254-0073, Japan[‡]Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-E4-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

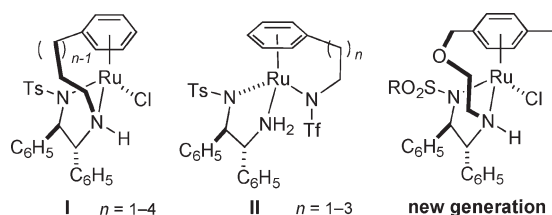
Supporting Information

ABSTRACT: Newly developed oxo-tethered Ru amido complexes (*R,R*)-**1** and their HCl adducts (*R,R*)-**2** exhibited excellent catalytic performance for both asymmetric transfer hydrogenation and the hydrogenation of ketonic substrates under neutral conditions without any cocatalysts to give chiral secondary alcohols with high levels of enantioselectivity.

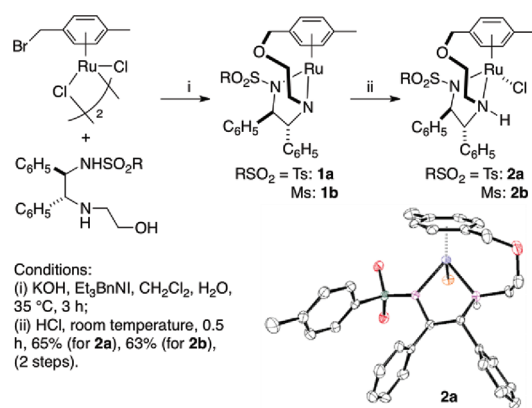
Catalytic asymmetric reduction of carbonyl compounds is one of the most sophisticated chiral multiplication methods in organic synthesis.¹ Significant progress has been made in the asymmetric transfer hydrogenation of aromatic ketones using 2-propanol or formate salts through the use of conceptually new chiral bifunctional hydrido-Ru(II) catalysts with monosulfonylated chiral diamines, RuH[(*R,R*)-Tsdpn](η^6 -arene) [TsDPN = TsNCH(C₆H₅)CH(C₆H₅)NH₂],² and an innovative reaction protocol has been realized as a practical tool that is complementary to asymmetric hydrogenation for accessing chiral secondary alcohols, even in chemical and pharmaceutical processes.³ Further intense research efforts to refine the prototype of bifunctional catalyst have led to the development of new catalytic systems displaying greater efficiency in terms of both reactivity and enantioselectivity.^{3,4} In particular, Wills' tethered catalysts (**I**), shown in Chart 1, are noteworthy because they show greater activities and are more stable than the original catalysts.⁵

Recently, structural modification of the catalyst prototype through changes in the chelating amine ligands or the formation of cationic amine complexes has been shown to cause facile activation of H₂, leading to practical asymmetric hydrogenation catalysts.^{6,7} We previously reported that triflylamide-tethered Ru–Tsdpn complexes (**II** in Chart 1), as well as their Rh and Ir

Chart 1



Scheme 1. Synthesis of Chiral Amido Catalysts (*R,R*)-**1** and Their HCl Adducts (*R,R*)-**2** and an ORTEP Drawing of (*R,R*)-**2a**



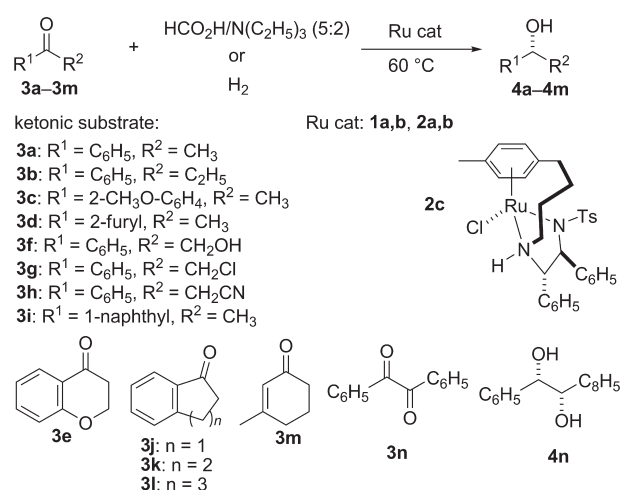
variants, serve as excellent catalysts for asymmetric hydrogenation of aromatic ketones but unfortunately not for transfer hydrogenation.⁸ We report here a new generation of heteroatom-tethered complexes, (*R,R*)-**1** and their HCl adducts (*R,R*)-**2** (Scheme 1), that exhibit excellent catalytic performance in terms of reactivity and selectivity for both asymmetric transfer hydrogenation and H₂ hydrogenation under neutral conditions without any cocatalyst.

Newly developed oxo-tethered Ru amido complexes **1a,b** and their HCl adducts **2a,b** (**a** = TsDPN derivatives; **b** = MsDPN derivatives), which were conveniently prepared by the one-pot reaction of a dimeric (η^6 -bromoxylene)Ru complex with monosulfonylated DPEN derivatives having a hydroxyalkyl chain, followed for **2** by treatment with HCl (Scheme 1; also see the Supporting Information), proved to be efficient chiral catalysts for the asymmetric reduction of ketones. The structure of complex (*R,R*)-**2a** was determined by X-ray crystallography to have a three-legged piano-stool configuration around the central metal, as shown in Scheme 1.

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Scheme 2. Asymmetric Reduction of Ketones



Asymmetric transfer hydrogenation of acetophenone (**3a**) with tethered complexes (*R,R*)-**2a,b** in an azeotropic mixture of HCO₂H and N(C₂H₅)₃ (Scheme 2) proceeded rapidly [substrate/catalyst (S/C) = 1000] in 3 h at 60 °C, giving the corresponding chiral (*R*)-alcohol in up to 97% ee (Table 1, runs 1 and 2). Catalyst (*R,R*)-**2a** maintained its catalytic ability after 4 days of reaction, showed an equal level of enantioselectivity at loadings as low as S/C = 30 000, and provided the highest activity among a series of (arene)Ru–Tsdpen complexes (run 3). In addition, the catalytic activity of **2a** was much higher than that of the Wills-type C4-tethered complex (*S,S*)-**2c**.^{5b,g}

A range of ketones, including propiophenone (**3b**) and *o*-methoxyacetophenone (**3c**), can be reduced to the corresponding secondary alcohols in high chemical yields with excellent ee's at relatively low catalyst concentration (S/C = 1000) (runs 6 and 7). Notably, the reduction of oxygen-functionalized ketones **3d** and **3e** gave the corresponding alcohols within 5 h with almost perfect enantioselectivities (runs 8 and 9). Other functionalized ketones, including α -hydroxy-, α -chloro-, and α -cyanoacetophenone (**3f–h**), were also reduced in a highly enantioselective manner to give quantitatively chiral products with 96, 97, and 95% ee, respectively, without any byproducts (runs 10–12). In the reduction of 1-acetonaphthone, the complex (*R,R*)-**2b** provided a better result than the Ts analogue (runs 13 and 14). (*R,R*)-**2b** also showed excellent enantiodiscrimination ability in the reaction with a seven-membered fused-ring aromatic ketone (**3l**; run 15), although the rate was low. The reaction of cyclic enone **3m** with S/C = 200 gave the corresponding allyl alcohol with 96% ee (run 16). 1,2-Diketone **3n** was also reducible at 60 °C with S/C = 10 000 in a DMF solution of HCOOH/N(C₂H₅)₃ containing (*R,R*)-**2a** to give chiral (*S,S*)-hydrobenzoin (**4n**) almost quantitatively with good diastereoselectivity (*dl:meso* = 97.2:2.8) and excellent ee (>99% ee).⁹

Encouraged by the marked increase in catalytic activity, which was possibly due to the introduction of electron-donating groups in the tether unit and the amino unit, we anticipated that increased basicity of the amine might render the amido-Ru complexes (*R,R*)-**1** and chloro-Ru complexes (*R,R*)-**2** catalytically active for the hydrogenation reaction without any modification.¹⁰ In fact, the hydrogenation of acetophenone in methanol containing the 16-electron amido complex (*R,R*)-**1a** (S/C = 500) at 60 °C

Table 1. Asymmetric Transfer Hydrogenation of Ketones Catalyzed by (*R,R*)-**1a**, (*R,R*)-**2a**, or (*S,S*)-**2c**^a

run	ketone	cat	S/C	time (h)	% yield ^b	% ee ^{c,d}
1	3a	2a	1000	3	>99	97 (<i>R</i>)
2		2b	1000	3	>99	95 (<i>R</i>)
3		2a	30000	96	95	97 (<i>R</i>)
4		2a	40000	72	75	97 (<i>R</i>)
5		(<i>S,S</i>)- 2c	40000	72	15	96 (<i>S</i>)
6	3b	2a	1000	24	>99	94 (<i>R</i>)
7	3c	2a	1000	24	>99	93 (<i>R</i>)
8	3d	2a	1000	5	>99	98 (<i>R</i>)
9	3e	2a	1000	5	>99	>99 (<i>R</i>)
10	3f	2a	1000	5	98	96 (<i>S</i>) ^e
11 ^f	3g	2a	1000	5	>99	97 (<i>S</i>)
12	3h	2a	1000	5	>99	95 (<i>R</i>)
13	3i	2a	1000	24	94	84 (<i>R</i>)
14		2b	1000	24	96	97 (<i>R</i>)
15	3l	2b	1000	24	85	98 (<i>R</i>)
16	3m	2a	200	6	94	96 (<i>R</i>)

^a Standard reaction conditions (S/C = 1000): substrate (5 mmol), catalyst (0.005 mmol), 5:2 formic acid/triethylamine azeotropic mixture (2.5 mL). ^b Determined by GC or ¹H NMR spectroscopy. ^c The ee was determined by GC analysis using a CHIRALSIL-DEX-CB capillary column, unless otherwise noted. ^d The major enantiomer was determined by the sign of optical rotation. ^e The ee was determined by HPLC analysis using a TCI MB-S column. ^f EtOAc was added as a cosolvent.

and 3.0 MPa H₂ proceeded smoothly to yield (*R*)-1-phenylethanol almost quantitatively with 95% ee, whereas the catalyst (*R,R*)-**2a** gave the product in only moderate yield (Table 2, runs 1 and 2). Various aromatic ketones can be hydrogenated with high chemical yield and satisfactory ee with S/C = 1000. A base-sensitive substrate, 4-chromanone (**3e**), and other fused-ring aromatic ketones, 1-indanone (**3j**) and 1-tetralone (**3k**), were also reduced using (*R,R*)-**1** or **2**, and the amido catalyst (*R,R*)-**1a** showed catalytic activities higher than and selectivities comparable to those of (*R,R*)-**2a** (runs 3, 4, and 6–9). The hydrogenation of α -hydroxyacetophenone **3f** using (*R,R*)-**2a** was almost complete within 18 h even with S/C = 5000, while the C4-tethered complex (*S,S*)-**2c** gave an unsatisfactory result (runs 10 and 11).

The hydrogenation ability of the tethered complexes was successfully applied to the reduction of lactone. The reaction of γ -butyrolactone with pressurized H₂ (5.0 MPa) was promoted by (*R,R*)-**2a** (2 mol %) in 2-propanol containing ^tBuOK (20 mol %) to yield 1,4-butanediol quantitatively after 48 h (Scheme 3).^{6g,11}

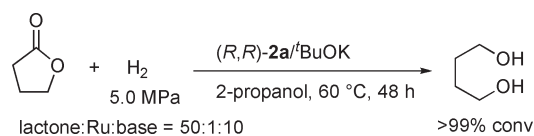
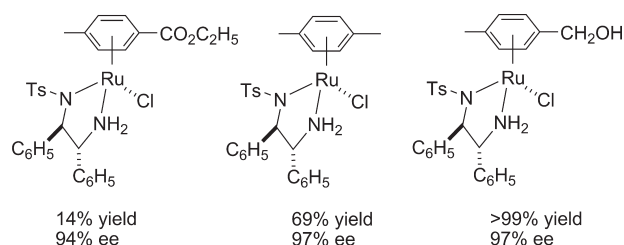
The remarkable improvement in the catalytic performance of the oxo-tethered Ru catalysts **1** and **2** in terms of reactivity, stability, and diversity depending on the hydrogen source might be explained by the delicate electronic tuning of cooperating ligands in the present catalysts. Separate experiments with non-tethered Ru–arene complexes for the transfer hydrogenation of acetophenone (Scheme 4) revealed that a complex containing electron-donating *p*-xylene exhibited a higher catalytic activity than a complex with an electron-withdrawing ester group, which is consistent with the results in preceding studies.^{3c,12} The introduction of a CH₂OH group on the η^6 -arene ligand resulted in complete conversion of the ketone with excellent enantioselectivity.

In addition, the use of the secondary amino unit in the TsDPEN ligand might enhance the electron density to give the

Table 2. Asymmetric Hydrogenation of Ketones Catalyzed by (R,R)-1a, (R,R)-2a, (R,R)-5a, or (S,S)-2c^a

run	ketone	cat	S/C	time, h	% yield ^b	% ee ^{c,d}
1	3a	1a	500	20	99	95 (R)
2		2a	500	20	58	90 (R)
3	3e	1a	1000	20	99	97 (R)
4		2a	1000	20	99	99 (R)
5		5a	1000	20	99	99 (R)
6	3j	1a	1000	18	97	98 (R)
7		2a	1000	18	59	98 (R)
8	3k	1a	1000	18	85	>99 (R)
9		2a	1000	18	52	>99 (R)
10	3f	2a	5000	18	99	93 (S) ^e
11		(S,S)-2c	5000	18	35	89 (R) ^e

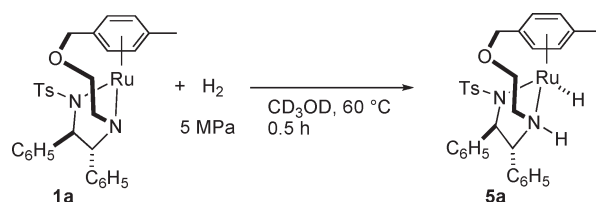
^a Standard reaction conditions (S/C = 1000): substrate (5 mmol), catalyst (0.005 mmol), MeOH (4.4 mL), H₂ (3.0 MPa). ^b Determined by GC or ¹H NMR spectroscopy. ^c The ee was determined by GC analysis using a CHIRALSIL-DEX-CB capillary column, unless otherwise noted. ^d The major enantiomer was determined by the sign of optical rotation. ^e The ee was determined by HPLC analysis using a TCI MB-S column.

Scheme 3. Asymmetric Hydrogenation of Lactone Catalyzed by Ruthenium Catalyst (R,R)-2a**Scheme 4. Asymmetric Hydrogenation of Acetophenone Catalyzed by Nontethered Ru Complexes^a**

^a Conditions: S/C = 500, 5:2 HCO₂H/N(C₂H₅)₃, 2 M, 30 °C, 24 h

facile activation of molecular hydrogen with the aid of the conjugated bases of alcohols and acids.^{6a,b} In fact, the reaction of amido complex **1a** with pressurized hydrogen under conditions that are otherwise similar to those in asymmetric hydrogenation except for the absence of ketones cleanly gave the corresponding hydrido-Ru complex **5a** almost quantitatively, as determined by NMR analysis (Scheme 5; also see the Supporting Information). The isolated hydride complex **5a** also exhibited the same catalytic performance as complex **1a** (Table 2, run 5).

These experimental data also strongly support the notion that the oxo-tethered Ru amido or chloride complexes exhibit excellent catalytic performance for both asymmetric transfer hydrogenation and hydrogenation of ketones. Since the bifunctional nature of the present tethered catalysts could be achieved without

Scheme 5. Formation of Hydrido-Ru Complex 5a by Treatment of Tethered Amido-Ru Complex 1a with H₂

further ligand modification, these two asymmetric reductions of ketones can be used in a complementary manner in organic synthesis. Rational design of the ligands that adjust the balance of electronic factors on the M/NH units in the bifunctional catalysts is crucially important for further exploitation of this unprecedented catalytic performance.

■ ASSOCIATED CONTENT

S Supporting Information. Results of asymmetric transfer hydrogenation using other substrates; results of an experiment comparing oxo-tethered complex (R,R)-2a and C4-tethered complex (S,S)-2c; preparative methods for Ru complexes; experimental procedures for asymmetric transfer hydrogenation and H₂ hydrogenation; NMR, GC, and HPLC data; [α]_D values for products; and X-ray crystallographic data for (R,R)-2a and (S,S)-2c (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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