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Aerobic oxidation with bifunctional molecular catalysts*

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Abstract: A new series of half-sandwich group 8 and 9 metal complexes bearing a metal/NH bifunctional moiety were synthesized from benzylic amines. The isolable Ir amide complexes serve as effective catalysts for aerobic oxidative transformation of secondary and primary alcohols into the corresponding ketones and esters under mild conditions. The aerobic oxidative kinetic resolution of racemic secondary alcohols with chiral bifunctional Ir catalysts was found to proceed smoothly under mild conditions with high selectivity. A novel imido-bridged dirhodium complex, which may be regarded as a dinuclear variant of the bifunctional mononuclear amide complexes, also proved to promote aerobic oxidation of a secondary alcohol and H_2.

Keywords: aerobic oxidation; alcohol oxidation; bifunctional catalysis; cooperating ligand; H_2 oxidation; molecular catalysts.

INTRODUCTION

Recently, much attention has been given to the design of bifunctional molecular catalysts based on the synergy effect of a Lewis acid and Brønsted base sites working in concert, to attain highly efficient molecular transformation for organic synthesis. We have developed conceptually new transition-metal-based bifunctional molecular catalyst bearing chiral chelating amine ligands for asymmetric reduction and enantioselective C–C and C–N bond formation [1]. This bifunctional molecular catalysis is unique and simple. In fact, the catalytic cycle for the asymmetric reduction includes only two active species, an amido complex and an amine complex with a metal/NH synergetic effect as shown in Scheme 1. During interconversion between both the catalyst and the intermediate, these amido/amine complexes have opposite acid–base properties around M–N bonds and work independently to activate the substrates, and therefore, the catalyst deactivation due to the acid–base neutralization or destructive aggregation can be minimized. This unique concept of the bifunctional transition-metal-based molecular catalysts leads to high reaction rates and excellent stereoselectivies because the reactions proceed through a tight-fitting assembly of the reactants and chiral catalysts. This bifunctional catalyst can also provide a wide substrate scope and applicability in organic synthetic chemistry. Although the forward reaction using hydrogen sources has been investigated as a useful reductive transformation and applied widely to organic synthetic procedures, the reverse reaction with the appropriate hydrogen acceptors, oxidative transformation, has remained unexplored. Herein, we focus on our recent progress in oxidative trans-

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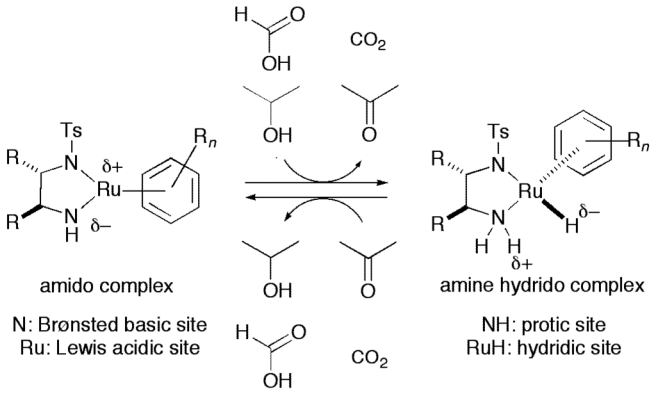


Scheme 1

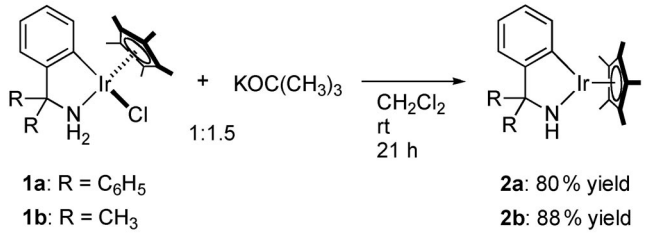
formation with bifunctional molecular catalysts based on mononuclear ruthenium, rhodium, and iridium complexes as well as newly developed dinuclear complex, bis(imido)-bridged dirhodium(III) complex, and their utilization to aerobic oxidation of alcohols, in which the oxygen molecule works as a suitable hydrogen acceptor.

BIFUNCTIONAL CATALYSIS OF MONONUCLEAR C–N CHELATING AMINE COMPLEXES

Synthesis and reactivities of new Cp*Ir amido and hydrido(amine) complexes bearing C–N chelate ligands

We developed a new series of bifunctional amido- and hydrido(amine)-Ir complexes with C–N chelate amine ligands derived from benzylic amines [2]. The starting neutral chloride complexes, Cp*IrCl[κ^2(*N*,*C*)-(NH_2CR_2-2-C_6H_4)] (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl; **1a**: R = C_6H_5, **1b**: R = CH_3), were readily prepared from the reaction of $[Cp^*IrCl_2]_2$ and primary benzylic amines ($C_6H_5CR_2NH_2$; R = C_6H_5 and CH_3) in the presence of sodium acetate in CH_2Cl_2 at room temperature. The products were fully characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. Analogous Rh and Ru complexes having C–N chelate ligands were also synthesized in a similar manner to the Cp*Ir complexes. Related cationic C–N chelate metallacycles have been investigated, but catalytically active amido and hydrido(amine) complexes have not been isolated [3].

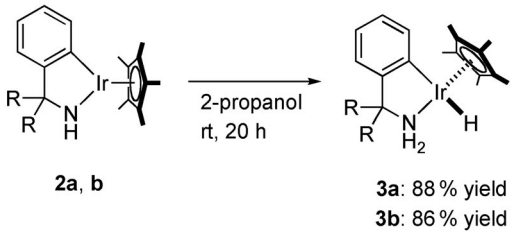
The cyclometalated amido-Ir complexes, Cp*Ir[κ^2(*N*,*C*)-($NHCR_2$-2-C_6H_4)] (**2a**: R = C_6H_5, **2b**: R = CH_3), were obtained as purple solids in good yields from the reaction of **1** with 1.5 equiv of $KOC(CH_3)_3$ in CH_2Cl_2 at room temperature (Scheme 2). Single-crystal X-ray crystallography of **2a** indicates that **2a** is a monomeric 16-electron neutral complex with a planar geometry around the metal center bearing Cp* and a C–N chelate ligand. The amido complex has a relatively short Ir–N bond,



Scheme 2

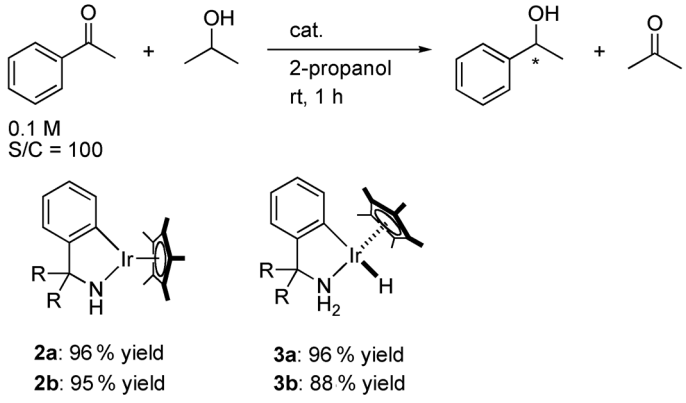
1.903(2) Å, compared with that of the Ir–NH_2 bond, 2.137 Å, in the chloro complex **1a**, as observed in analogous amido- and (hydrido)amine-Ru complexes.

The isolable 16-electron amido complexes **2** were found to react readily with 2-propanol at ambient temperature, leading to the 18-electron hydrido(amine) complexes, Cp*IrH[κ^2(*N*,*C*)-{NH_2CR_2-2-C_6H_4}] (**3a**: R = C_6H_5, **3b**: R = CH_3), as previously observed in Ru- and Ir-Ts-diamine complexes (Scheme 3) [4].



Scheme 3

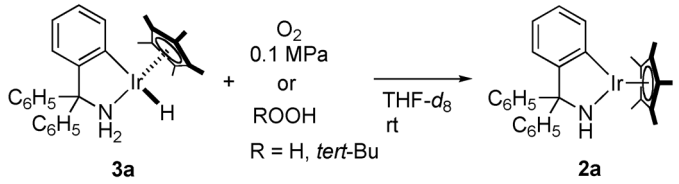
The hydrido complexes **3** were found to be thermally stable under an Ar atmosphere, and reacted smoothly with acetone in CH_2Cl_2 at room temperature to give 2-propanol. As expected from the stoichiometric reactions, the isolable amido complexes **2** and hydrido(amine) complexes **3** catalyzed the transfer hydrogenation of acetophenone in 2-propanol at room temperature to give 1-phenylethanol in 88–98 % yield after 1 h (Scheme 4). These results indicate that amido-Ir complexes with C–N chelating ligands act as promising bifunctional catalysts for highly efficient transfer hydrogenation.



Scheme 4

Notably, the hydrido(amine)-Ir complexes **3** reacted rapidly with molecular oxygen under mild conditions to generate the corresponding amido-Ir complexes **2** [5] as shown in Scheme 5. Monitoring a solution of **3a** in THF-d_8 under air at room temperature by ^{1}H NMR spectroscopy showed a rapid decrease in the intensity of a hydride signal at –13.1 ppm and an increase in the characteristic signal due to the N–H moiety of **2a** at 8.37 ppm, indicating the smooth conversion to the amido complex by the action of O_2. Other oxidants like hydroperoxides also promoted the transformation to **2a**. The reaction of **3a** with an equimolar amount of H_2O_2 in THF-d_8 for 24 h gave **2a** in 95 % yield in addition to a detectable amount of H_2O. The O–O bond cleavage of peroxides with the hydrido complex **3a** was also clearly demonstrated in the treatment of *tert*-BuOOH, which afforded **2a** and *tert*-BuOH. Although the

precise mechanism of the formation of **2a** from **3a** in the presence of O_2 has remained unclear, these findings as well as recently reported results [6] imply that the reaction of **3a** with O_2 may proceed through O_2 insertion into the metal–hydride bond to form an amine–hydroperoxo complex, followed by the release of **2a** and H_2O_2. The H_2O_2 product then reacts with **3a** to provide **2a** and water.

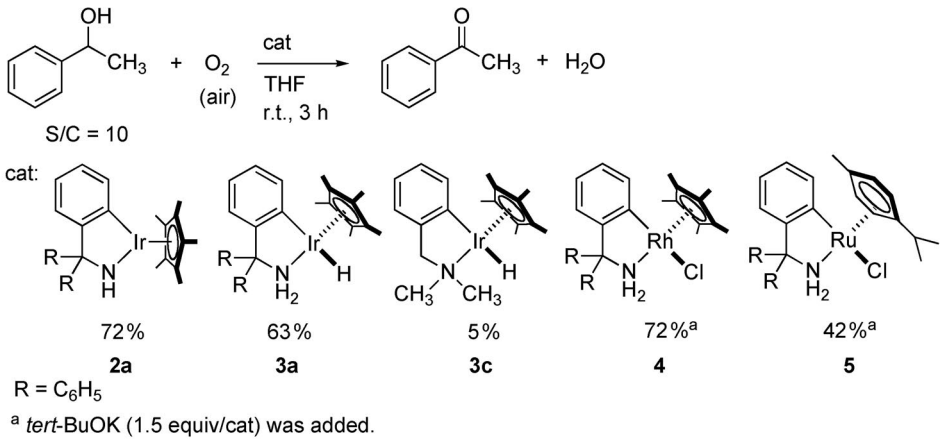


Scheme 5

Aerobic oxidation of secondary and primary alcohols

On the basis of a combination of the reactions shown in Schemes 3 and 5, we successfully developed the aerobic oxidation of alcohols with chiral bifunctional Cp*Ir, Cp*Rh, and (η^6-arene)Ru catalysts [5,7]. Because the employment of molecular oxygen as a hydrogen acceptor in alcohol oxidation is especially attractive from economical and environmental points of view, a wide variety of homogeneous and heterogeneous systems [8] based on transition metals have been explored; however, limited examples of Rh- and Ir-catalyzed reaction have been reported [6,9,10].

The Ir, Rh, and Ru complexes bearing C–N chelate ligands catalyzed the aerobic dehydrogenative oxidation of 1-phenylethanol under identical conditions (Scheme 6). The reaction of 1-phenylethanol proceeded smoothly under atmospheric pressure of air at 30 °C in THF containing amido-Ir complex **2a** with a substrate/catalyst (S/C) ratio of 10 to give acetophenone in 72 % yield after 3 h. The hydrido(amine)-Ir complex with the metal/NH bifunctional unit (**3a**) also afforded the oxidation product acetophenone, whereas the hydrido complex **3c** bearing an *N*,*N*-dimethylamino group did not exhibit catalytic activity under otherwise identical conditions, indicating that the M/NH bifunction is also crucial for O_2 activation and that the aerobic dehydrogenation proceeds through the interconversion between the amine/amido catalyst intermediates. Binary catalyst systems, including the chloro(amine)-Rh and -Ru complexes (**4** and **5**) and $KOC(CH_3)_3$, were applicable to the aerobic oxida-



Scheme 6

tion. Other 1-phenylethanols with substituents on the arene ring, sterically congested diphenylmethanol, and an aliphatic secondary alcohol are convertible into the corresponding ketones by using the amido complex **1a** as shown in Table 1.

Table 1 Aerobic oxidation of secondary alcohols with **2a**.[a]

Entry	Substrate	Product	Yield (%)
1	$C_6H_5CH(OH)CH_3$	$C_6H_5COCH_3$	72
2	$4\text{-}CH_3OC_6H_4CH(OH)CH_3$	$4\text{-}CH_3OC_6H_4COCH_3$	62
3	$4\text{-}ClC_6H_4CH(OH)CH_3$	$4\text{-}ClC_6H_4COCH_3$	55
4	$C_6H_5CH(OH)C_6H_5$	$C_6H_5COC_6H_5$	62
5	$C_6H_5CH_2CH_2CH(OH)CH_3$	$C_6H_5CH_2CH_2COCH_3$	87

[a]Reaction conditions: **2a** (0.10 mmol), alcohol (1.0 mmol), THF (1 ml), air (0.1 MPa), 30 °C, 3 h.

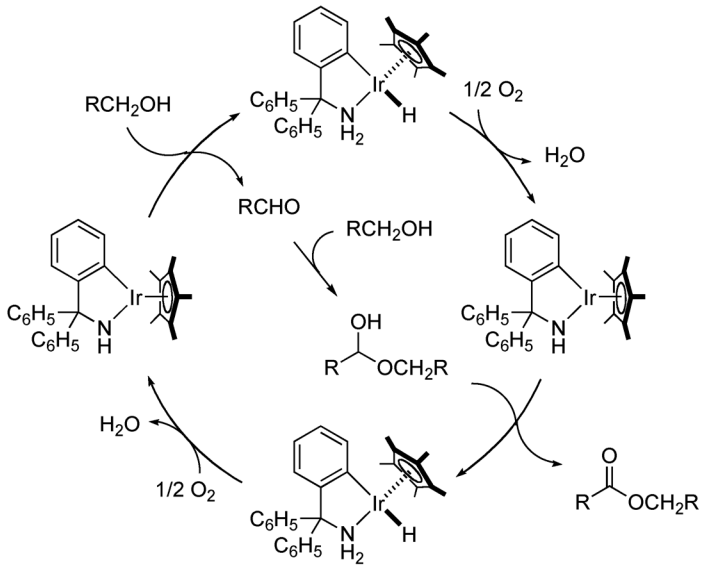
The reaction of primary alcohols under identical conditions afforded the oxidative dimerization product, esters [11]. When a mixture of benzyl alcohols containing combined catalyst of the chloro complex **1a** with an equimolar amount of $KOC(CH_3)_3$ in THF was stirred under air at 30 °C, the corresponding benzyl benzoate derivatives were obtained in a range of 62–64 % yields (entries 1–3, Table 2). The oxidation of 1,2-benzenedimethanol also afforded phthalide in 72 % yield by an intramolecular esterification (entry 4).

Table 2 Aerobic oxidative esterification of primary alcohols.[a]

Entry	Substrate	Product	Time (h)	Yield (%)
1	$C_6H_5CH_2OH$	$C_6H_5CO_2CH_2C_6H_5$	18	64
2	$p\text{-}ClC_6H_4CH_2OH$	$p\text{-}ClC_6H_4CO_2CH_2(p\text{-}ClC_6H_4)$	3	62
3	$p\text{-}CH_3C_6H_4CH_2OH$	$p\text{-}CH_3C_6H_4CO_2CH_2(p\text{-}CH_3C_6H_4)$	18	64
4	$1,2\text{-}(HOCH_2)_2C_6H_4$	phthalide	3	72

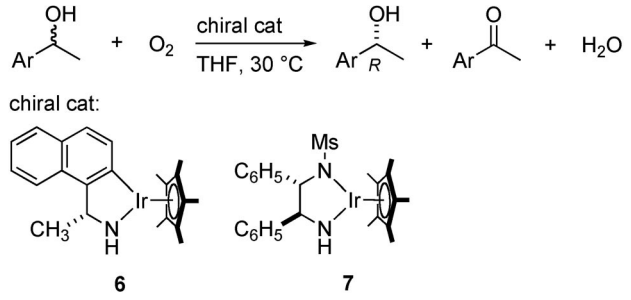
[a]Reaction conditions: **1a** (0.10 mmol), $KOC(CH_3)_3$ (0.12 mmol), alcohol (1.0 mmol), THF (1 ml), air (0.1 MPa), 30 °C.

To account for the dehydrogenative process with the bifunctional catalysts, a plausible mechanism is shown in Scheme 7. In the presence of O_2, the oxidation of benzyl alcohol takes place smoothly to give benzaldehyde. Subsequent attack of the remaining alcohol affording the hemiacetal and its ready conversion into the ester is accomplished by the second oxidation.



Scheme 7

This aerobic oxidation of alcohols is more appealing when applied to the kinetic resolution of racemic secondary alcohols with chiral amido catalysts (Scheme 8) [12,13]. The efficiency is significantly influenced by the redox properties of the alcohols and the reaction conditions as well as the chiral catalyst performance.

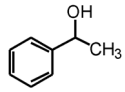
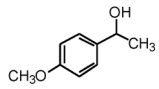
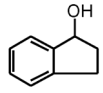
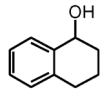


Scheme 8

When a THF (1.0 M) solution of racemic 1-phenylethanol with the chiral Ir complex, **6** derived from (*R*)-1-naphthylethylamine (S/C = 10) was treated with air at 30 °C for 4 h, (*R*)-1-phenylethanol was recovered with a 48 % yield and 14 % ee (Scheme 8, Table 3 entry 1). Noticeably, the use of the chiral amido Ir complex bearing an N-sulfonylated 1,2-diphenylethylenediamine (DPEN) ligand, Cp*Ir[(*S*,*S*)-Msdpen] (**7**) (Ms = methanesulfonyl), significantly improved the enantiomer discrimination ability, and (*R*)-1-phenylethanol was recovered in 44 % yield and 84 % ee with a k_f/k_s ratio of 12.6, although a prolonged reaction time was necessary for completion (entry 2). Further improvement in the stereochemical outcome of the reaction was possible when the reaction was carried out under diluted conditions. The desired *R*-alcohol with 98 % ee was recovered in 48 % yield, the k_f/k_s value being up to 90 (entry 3). A 1-phenylethanol derivative having an electron-donating CH_3O group at the para position was efficiently resolved with catalyst **7** (entry 4). Similarly, the *R*-enantiomers with >99 % ee and

with 46–50 % yields were readily obtainable from the reactions of 1-indanol and 1-tetralol at ambient temperature (entries 5 and 6).

Table 3 Aerobic oxidative kinetic resolution of secondary alcohols.[a]

Entry	Alcohol	Conc. (M)	Cat.	Time (h)	Unreacted alcohol		
					Recovery (%)[b]	ee (%)[c]	k_f/k_s
1		1.0	**6**	4	48	14	1.5
2		1.0	**7**	22	44	84	12.6
3		0.2	**7**	38	48	98	91.3
4		0.2	**7**	19	38	98	17.2
5		0.1	**7**	6	50	>99	>100
6		0.1	**7**	6.5	46	>99	77.6

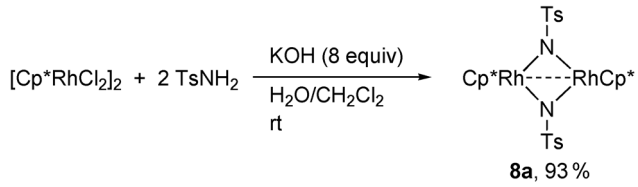
[a]Reaction conditions: The reaction was carried out with a solution of alcohol (1.1 mmol) in THF and an S/C ratio of 10 under air.
[b]Recovered starting material; determined by GC, using durene as an internal standard.
[c]Determined by HPLC on a Daicel Chiralcel OD column.
[d]*tert*-BuOK (1.5 equiv) was added.

EXTENSION TO DINUCLEAR BIFUNCTIONAL CATALYSTS BEARING METAL–NITROGEN BOND

We next envisioned that the bifunctional effect of the amido complex would also be operative in imido-bridged dinuclear half-sandwich complexes with M–N bonds. Exploration into the catalysis of these complexes had been hampered by their various decomposition processes such as imide transfer reactions. However, our recent studies revealed that the electron-withdrawing sulfonyl group stabilizes the imido-bridged dinuclear complexes [14,15], which allows us detailed study of the bifunctional properties of the M–N bond therein. We describe here the reactivities of the imido-bridged dirhodium(III) complex and the application to catalytic aerobic oxidation of H_2 and alcohol [16].

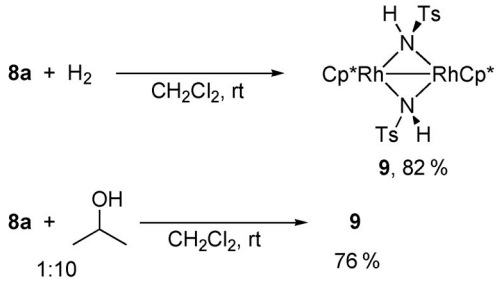
Synthesis and hydrogenation of sulfonylimido-bridged dirhodium(III) complex

The bis(imido)-bridged dirhodium(III) complex **8a** was obtained in a similar manner to the iridium analog [(Cp*Ir)$_2$(μ-NTs)$_2$] (**8b**; Ts = $SO_2C_6H_4CH_3$-*p*) [14]. In fact, the reaction of [Cp*RhCl$_2$]$_2$ with 2 equiv of $TsNH_2$ in the presence of KOH smoothly took place to afford **8a** in excellent yield (Scheme 9). The coordinatively unsaturated, yet air- and moisture-stable complex **8a** has been characterized by ^{1}H NMR spectroscopy, elemental analysis, and X-ray crystallography.



Scheme 9

The bis(imido)-bridged dirhodium(III) complex **8a** reacted with H_2 (1 atm) in CH_2Cl_2 for 24 h at room temperature to afford the bis(amido)-bridged dirhodium(II) complex **9** in 82 % yield as shown in Scheme 10. The NH signals at 5.46 and 2.53 ppm in the ^{1}H NMR spectrum of **9** were identified by their exchange with added D_2O. An X-ray diffraction analysis of **9**·$TsNH_2$, which has been obtained by recrystallization of **9** in the presence of $TsNH_2$, revealed the presence of intra- and intermolecular hydrogen bonds between the amido protons and the sulfonyl O atoms. The Rh–Rh distance in **9** is much shorter than that in **8a** (2.6004(12) vs. 2.7992(4) [17] Å) in agreement with the presence of an Rh(II)–Rh(II) single bond. In this reaction, H_2 is formally converted into two amido protons and two electrons for the reduction of the dirhodium(III) core in **8a**. Such H_2 oxidation on dinuclear platforms remains quite rare [18].

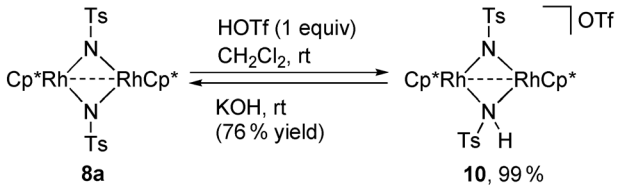


Scheme 10

The amido complex **9** was also obtained upon treatment of **8a** with an excess of 2-propanol (Scheme 10). The generation of two NH protons associated with two-electron reduction of the metal center is in sharp contrast with the dehydrogenation of primary and secondary alcohols by unsaturated mononuclear amido complexes, which leads to the formation of hydrido–amine complexes without formal reduction of the metal, as described above.

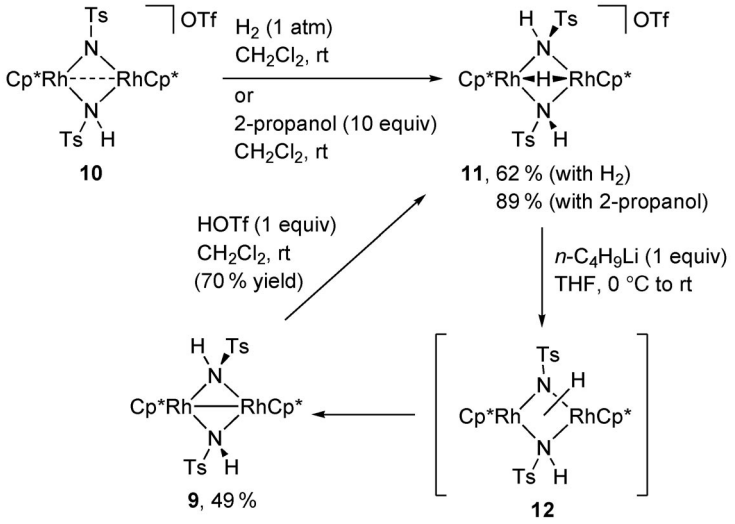
Protonation, hydrogenation, and deprotonation network of amido- and imido-bridged complexes

The rhodium complex **8a** underwent N-protonation with an equimolar amount of triflic acid to give the cationic amido- and imido-bridged dirhodium complex **10** despite the presence of the electron-withdrawing sulfonyl group on the imido nitrogen (Scheme 11). The ^{1}H NMR spectrum of **10** exhibits an NH signal at 8.46 ppm, while the IR spectrum shows an NH band at 3160 cm^{-1}. The Brønsted acidity of the NH proton in **10** was demonstrated by facile deprotonation with KOH to regenerate the parent bis(imido)-bridged complex **8a** in good yield.

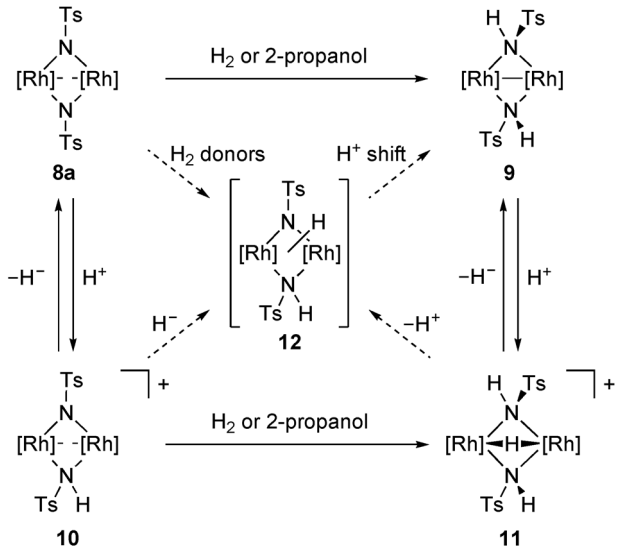


Scheme 11

In contrast to the reaction of **8a** with H_2, simple heterolysis of H_2 took place when the cationic (amido)(imido)dirhodium(III) complex **10** was treated with H_2, giving the (hydrido)bis(amido)dirhodium(III) complex **11** (Scheme 12). 2-Propanol also worked as a hydrogen donor to provide **11**. The ^{1}H NMR spectrum of **11** exhibits a triplet ascribed to the bridging hydrido ligand at –9.20 ppm ($^1J_{RhH}$ = 23.3 Hz) as well as two NH singlets at 6.54 and 5.58 ppm, which indicate the anti orientation of the two bridging amido ligands in **11**. As expected, reversible protonation of the bis(amido)dirhodium(II) complex **9** provided an alternative route to **11**. Since only the amido protons in **11** undergo H–D exchange upon treatment with D_2O, deprotonation of **11** to **9** would occur by the initial loss of the NH proton to give the hydrido–amido–imido complex **12** as a possible intermediate. Subsequent proton transfer from the metal to the Brønsted basic imido nitrogen would afford **9** with formal reduction of $Rh(III)_2$ to $Rh(II)_2$. We have recently observed a similar proton migration in the mono(sulfonylimido)-bridged diiridium complex [Cp*IrCl(μ-H)(μ-NMs)IrCp*] (Ms = SO_2CH_3), which is triggered by the coordination of carbon monoxide [15]. In accordance with the facile proton shift, hydride addition to **10** with an equimolar amount of $LiBH(C_2H_5)_3$ also gave the bis(amido) complex **9** immediately. These observations, summarized in Scheme 13, imply that the intermediate **12** may also be generated by the heterolysis of H_2, as well as dehydrogenative oxidation of 2-propanol, on **8a**.



Scheme 12



Scheme 13

The density functional theory (DFT) calculations for the reaction of the mesylimido analog of **8a** $[(Cp^*Rh)_2(\mu_2\text{-}NMs)_2]$ (**8a'**) and H_2 revealed that heterolytic cleavage of H_2 assisted by the sulfonyl O atom (Chart 1, a) is a favorable pathway rather than the direct addition of H_2 to the Rh–N bond (b). Noteworthy is the similarity between the six-membered pericyclic transition state in this pathway and that proposed in related H_2 heterolysis, e.g., by mononuclear amido complexes with a solvent alcohol molecule (Chart 1, c) [19]. The proton relay from the sulfonyl O atom to the imido N atom and the following spontaneous hydride migration in the hydride–amide intermediate **13** highlight the significance of the Brønsted basicity of the two bridging sulfonylimido nitrogen atoms in this transformation.

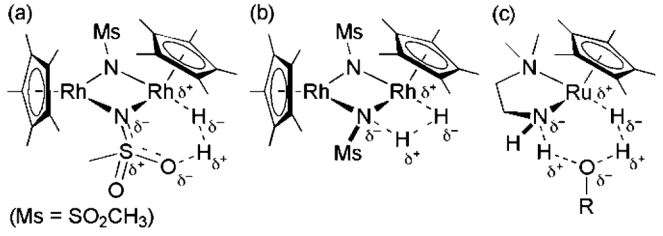
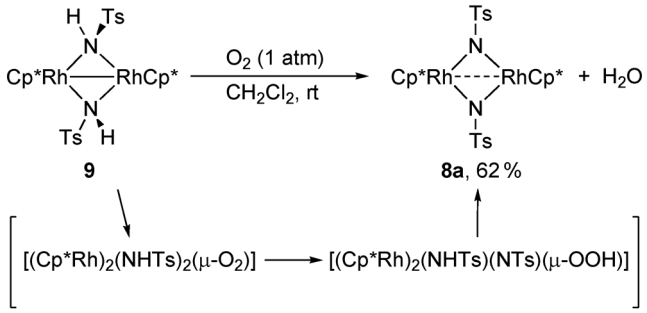


Chart 1

Reaction of bis(amido)rhodium(II) complex with O_2

The bis(amido)-bridged dirhodium(II) complex **9** rapidly reacted with O_2 to form the bis(imido)-bridged dirhodium(III) complex **8a** and water as shown in Scheme 14. Although no intermediate has yet been observed, the oxidation seems to occur via initial insertion of O_2 into the Rh(II)–Rh(II) bond in **9** followed by intramolecular proton shift from the amido ligand to the μ-peroxo ligand (Scheme 14). Regeneration of the bis(imido) complex **8a** from this hydroperoxo intermediate may be explained by scission of the Rh–OOH bond aided by the NHTs proton to yield H_2O_2, which reacts with **9** to give **8a** and H_2O, as described above.

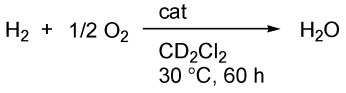


Scheme 14

Catalytic aerobic oxidation of H_2 and alcohol

The facile redox interconversion between **8a** and **9** (Schemes 10 and 14) could be applied to catalytic aerobic oxidation of H_2 and alcohols. When a CD_2Cl_2 solution of **8a** was treated with a 1:1 mixture of H_2 and O_2 (total pressure: 1 atm), water was produced catalytically (Table 4). In the reaction mixture, the sole rhodium species detectable by ^{1}H NMR spectroscopy is the bis(imido) complex **8a**, suggesting that the rate-determining step is the hydrogenation of **8a**. The turnover number seems limited by consumption of the gases and mass transfer since the rate of the reaction was revived upon addition of H_2 and O_2 (Fig. 1).

Table 4 Aerobic oxidation of H_2.



cat	TON[a]
8a	9 (26)[b]
8b	0
$[Cp^*RhCl_2]_2$	0

[a]Defined as moles of H_2O per mole of the catalyst, and determined by ^{1}H NMR spectroscopy.
[b]After 169 h.

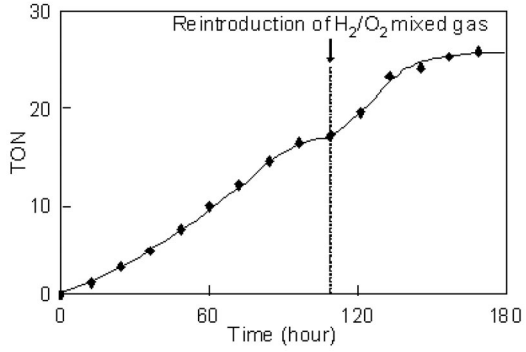
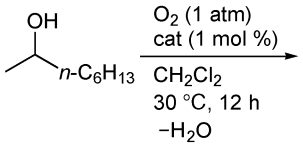


Fig. 1 Time course for the catalytic aerobic oxidation of H_2 with **8a**. TON is defined as moles of H_2O per mole of the catalyst.

Although such H_2 oxidation with O_2 promoted by homogeneous catalysts itself is not directly related to the practical energy production, it may provide some clue to the development of proton-coupled electron-transfer catalysts with high efficiency and reversibility. The aerobic H_2 oxidation shown in Table 4 is achieved by direct interconversion between the imido complex **8a** and the amido complex **9** without hydrido ligands. Lacking a facile hydrogenation process, the iridium analog **8b** and a rhodium complex $[Cp^*RhCl_2]_2$ without bridging imido ligands did not catalyze the oxidation at all.

The sulfonylimido-bridged dirhodium complex **8a** also catalyzes the aerobic dehydrogenative oxidation of alcohols. Reaction of 2-octanol with O_2 (1 atm) proceeded in the presence of 1 mol % of **8a** at 30 °C to give 2-octanone as shown in Table 5. Again, the iridium complex **8b** and a rhodium complex $[Cp^*RhCl_2]_2$ without bridging imido ligands did not show any catalytic activity, indicating that the reaction occurs via the imido–amido interconversion shown in Schemes 10 and 14. To the best of our knowledge, **8a** represents the first well-defined dinuclear catalyst for this reaction without fragmentation throughout the catalysis.

Table 5 Aerobic oxidation of alcohol.



cat	TON[a]
8a	15
8b	0
$[Cp^*RhCl_2]_2$	0

[a]Determined by GC.

CONCLUSIONS

We have demonstrated that the C–N chelate complexes facilitate aerobic oxidation of alcohols under mild conditions. The oxidative transformation relies on the facile interconversion between amido and amine complexes with a bifunctional M–N unit. The bifunctional catalysis has been extended to the dinuclear complexes bearing M–N bonds, which also proved to promote the oxidation of H_2 and alcohols using O_2 as a hydrogen acceptor. These reactions provide a novel environmentally benign process with minimal organic waste.

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