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Aerobic Oxidation of Alcohols with Bifunctional Transition-Metal Catalysts Bearing C–N Chelate Ligands

Sachiko Arita, Takashi Koike, Yoshihito Kayaki, and Takao Ikariya*[a]

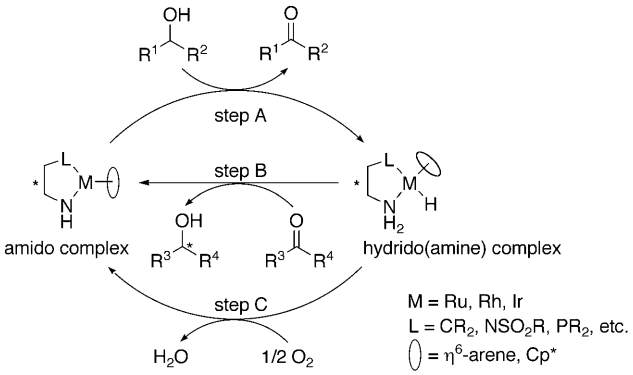
Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: The aerobic oxidation of alcohols with a family of bifunctional Ir, Rh, and Ru complexes bearing C–N chelating ligands derived from primary benzylic amines was investigated. The isolable amido–Ir complexes [Cp*Ir{κ^2-(*N*,*C*)-(NHCR$_2$-2-C$_6$H$_4$)}] (R = C$_6$H$_5$, CH$_3$; Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) effected the oxidation of secondary alcohols smoothly under atmospheric pressure of air at 30 °C in THF to give the corresponding ketones in good yields. The hydrido(amine)–Ir complexes [Cp*IrH{κ^2(*N*,*C*)-(NH$_2$CR$_2$-2-C$_6$H$_4$)}] and the combined catalyst system involving the chloro(amine)–Ir complex [Cp*IrCl{κ^2(*N*,*C*)-(NH$_2$CR$_2$-2-C$_6$H$_4$)}] and KOC(CH$_3$)$_3$ were also found to be effective catalysts, whereas the tertiary amine complex [Cp*IrCl{κ^2(*N*,*C*)-(N(CH$_3$)$_2$CH$_2$-2-C$_6$H$_4$)}], which does not have a metal/NH moiety, did not show catalytic activity. The employment of primary alcohols in the aerobic reaction with the Cp*IrCl complex and KOC(CH$_3$)$_3$ resulted in the formation of esters through oxidative dimerization.

Keywords: alcohols · homogeneous catalysis · iridium · oxidation · rhodium

Introduction

Bifunctional molecular catalysts based on a metal/NH synergy effect are now realized to be one of the most powerful and practical tools for attaining highly efficient molecular transformations.[1] These include asymmetric reduction of polar functional groups and enantioselective C–C and C–N bond formation. Among the systems developed to date, transfer hydrogenation has considerable potential in organic synthesis. Hydrogen transfer between secondary alcohols and ketones can proceed reversibly through interconversion of the real catalysts, the amido and hydrido(amine) complexes (Scheme 1). The amido complex readily dehydrogenates alcohols to generate the hydrido(amine) complex and ketones (step A). The resulting hydrido(amine) complex can activate the carbonyl group of ketone substrates by aid of the acidic NH proton, thus leading to the amido complex and secondary alcohols (step B). This reversibility is also applicable to the oxidation of alcohols in the presence of appropriate hydrogen acceptors such as ketones and α,β-unsaturated carbonyl compounds.[2]



Scheme 1. Hydrogen-transfer mechanism based on the metal/NH bifunctionality. Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl.

Recently, we developed a new series of bifunctional amido– and hydrido(amine)–Ir complexes with C–N chelate amine ligands derived from benzylic amines, [Cp*Ir{κ^2-(*N*,*C*)-(NHCR$_2$-2-C$_6$H$_4$)}] (**1a**: R = C$_6$H$_5$; **1b**: R = CH$_3$) and [Cp*IrH{κ^2(*N*,*C*)-(NH$_2$CR$_2$-2-C$_6$H$_4$)}] (**2a**: R = C$_6$H$_5$; **2b**:

[a] S. Arita, Dr. T. Koike, Dr. Y. Kayaki, Prof. Dr. T. Ikariya
Department of Applied Chemistry
Graduate School of Science and Engineering
Tokyo Institute of Technology
O-okayama 2-12-1, Meguro-ku, Tokyo 152-8552 (Japan)
Fax: (+81) 3-5734-2637
E-mail: tikariya@apc.titech.ac.jp

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R = CH_3).[3] The isolable Cp*Ir complexes **1** and **2** were found to effect the catalytic transfer hydrogenation of acetophenone. Notably, the Cp*Ir(C–N) complexes with electron-donating ligands showed greater activity than the Cp*Ir(Ts–diamine) catalyst system (Ts = *p*-toluenesulfonyl). Furthermore, the hydrido(amine)–Ir complexes **2** reacted rapidly with molecular oxygen under mild conditions to generate the corresponding amido–Ir complexes **1**, as represented by step C in Scheme 1.[4,5] On the basis of a combination of steps A and C, we successfully developed the aerobic oxidative kinetic resolution of racemic 1-aryl ethanol derivatives with chiral bifunctional Cp*Ir, Cp*Rh, and (η^6-arene)Ru catalysts.[4] Because the employment of molecular oxygen as a hydrogen acceptor in alcohol oxidation is especially attractive from economic and environmental points of view, a wide variety of homogeneous and heterogeneous systems[6] based on transition metals such as V,[7] Ru,[8] Co,[9] Pd,[10] Pt,[11] Cu,[12] and Au[13] have been explored; however, limited examples of Rh-[14] and Ir-catalyzed[4,5,15] reactions have been previously reported.

Our findings encouraged us to develop effective bifunctional catalysts bearing C–N ligands for the aerobic oxidation of alcohols. Herein, we report that a series of half-sandwich Group 8 and 9 metal complexes derived from benzylic amines serve as effective catalysts for the oxidative transformation of secondary and primary alcohols into the corresponding ketones and esters under mild conditions.

Results and Discussion

Synthesis of Cp*Rh and (*p*-cymene)Ru Complexes Bearing C–N Chelate Ligands

The catalyst precursors of Rh and Ru complexes with C–N chelate ligands were synthesized according to our previous report on related Cp*Ir complexes.[3,16] The reaction of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ with tritylamine or cumylamine in the presence of sodium acetate in THF at room temperature led to the formation of the metallacycles [Cp*RhCl{κ^2(*N*,*C*)-(NH_2CR_2-2-C_6H_4)}] (**4a**: R = C_6H_5; **4b**: R = CH_3), which were isolated as orange and red crystals in 89–99% yield. When the cyclometalation of the benzylic amines with $[RuCl(\mu\text{-}Cl)(p\text{-cymene})]_2$ was conducted at 60 °C in acetonitrile containing a slight excess of sodium acetate, the corresponding ruthenacycles, [RuCl{κ^2(*N*,*C*)-(NH_2CR_2-2-C_6H_4)}(*p*-cymene)] (**5a**: R = C_6H_5; **5b**: R = CH_3), were obtained in 61 and 45% yield, respectively. The isolable Rh and Ru complexes **4** and **5** were fully characterized by NMR spectroscopy and elemental analysis (see Experimental Section). The ^{1}H NMR spectrum of **4a** in CD_2Cl_2 exhibits a set of two doublets due to the NH_2 protons at 4.19 and 5.25 ppm with a geminal coupling constant of 10.0 Hz, which indicates the chelating structure of the amine ligand. The NH_2 protons of **4b** were observed as broad peaks at lower chemical shifts of 3.09 and 3.93 ppm. A similar trend was observed for the Ru complexes **5a** and **5b**. The formation of the C–Rh bond in **4a** and **4b** was further evidenced by the ^{103}Rh-coupled ^{13}C{^{1}H} NMR signals at 171.0 ($^1J_{C,Rh}$ = 30.7 Hz) and 167.5 ppm ($^1J_{C,Rh}$ = 29.7 Hz), respectively.

The molecular structures of the Rh complexes **4a** and **4b** in the solid state were confirmed by X-ray crystallographic analysis (Table 1). The ORTEP depictions of **4a** and **4b** are shown in Figures 1 and 2, along with the principal bond lengths and angles. Both complexes have distorted tetrahedral geometry with the Cp*, chloro, and C–N chelate ligands, as observed in the analogous Ir complexes.[3] A slight increase in the Rh–N bond length of **4a** (2.134 Å) with respect to that of **4b** (2.116 Å) may reflect the greater steric effect or the weaker electron-donating property of the phenyl substituents on the C–N chelate ligand relative to

Table 1. Crystallographic data for **4a** and **4b**.[a]

	4a·CH_2Cl_2	**4b**·$^1/_4$ $C_6H_5CH_3$
Empirical formula	$C_{30}H_{33}NCl_3Rh$	$C_{20.75}H_{29}NClRh$
M_r	616.86	430.82
Crystal color	orange	red
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$ (#19)	$C2/c$ (#15)
a [Å]	11.5625(19)	36.34(2)
b [Å]	11.9338(11)	10.438(6)
c [Å]	20.315(3)	22.023(13)
β [°]		107.287(6)
V [Å^3]	2803.2(7)	7976(8)
Z	4	16
D_{calcd} [g cm^{-3}]	1.462	1.435
F_{000}	1264.00	3560.00
$\mu(Mo_{K\alpha})$ [cm^{-1}]	9.128	9.898
No. of reflections measured	21908	42014
No. of unique reflections	6316	9122
No. of variables	332	465
$R1$ ($I > 2\sigma(I)$)	0.0597	0.0572
$wR2$ (all reflections)	0.1614	0.1257
GOF on F^2	1.001	0.995

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

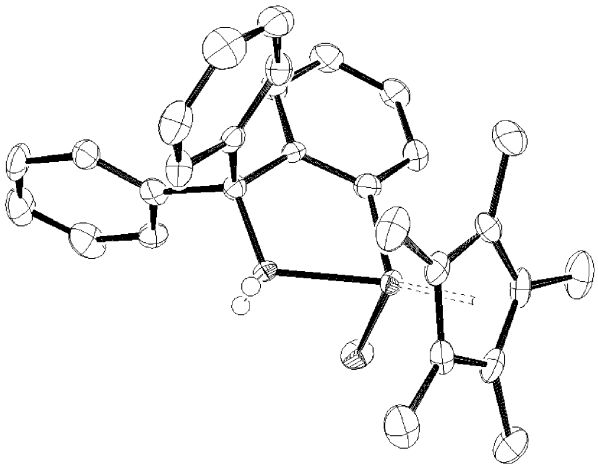

Figure 1. Molecular structure of [Cp*RhCl{κ^2(*N*,*C*)-($NH_2C(C_6H_5)_2$-2-C_6H_4)}]·CH_2Cl_2 (**4a**·CH_2Cl_2). The solvent molecule and hydrogen atoms other than the amine protons are omitted for clarity, and ellipsoids are drawn at the 50% probability level.

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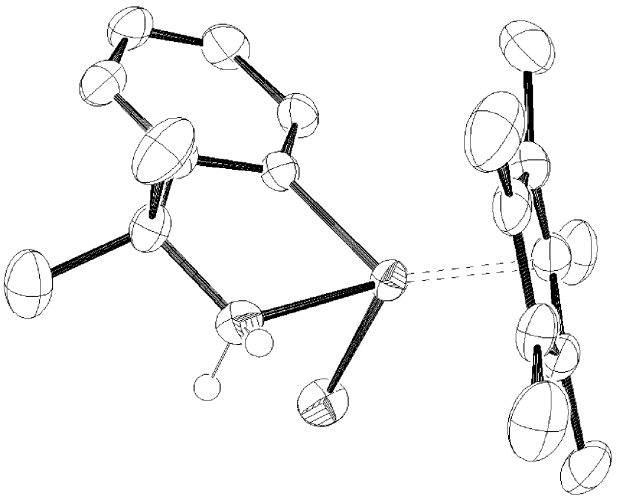
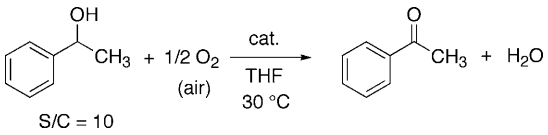


Figure 2. Molecular structure of [Cp*RhCl{κ^2(*N*,*C*)-($NH_2C(CH_3)_2$-2-C_6H_4)}]·$^1/_4$ $C_6H_5CH_3$ (**4b**·$^1/_4$ $C_6H_5CH_3$). Only one of the two independent molecules is shown. The solvent molecule and hydrogen atoms other than the amine protons are omitted for clarity, and ellipsoids are drawn at the 50% probability level.

the methyl substituents. The increased steric demands can also be seen in the N–Rh–C bite angle of **4a** (79.08°), which is larger than that of **4b** (78.35°).

Aerobic Oxidation of Secondary Alcohols

The Ir, Rh, and Ru complexes bearing C–N chelate ligands catalyzed the aerobic dehydrogenative oxidation of 1-phenylethanol under identical conditions [Eq. (1)]. Representative results are shown in Table 2. The reaction of 1-phenylethanol proceeded smoothly under atmospheric pressure of air at 30°C in THF containing amido–Ir complexes **1** with a substrate/catalyst (S/C) ratio of 10 to give acetophenone in 66–72% yield after 3 h (Table 2, entries 1 and 2). The phenyl substituent on the α-carbon atom bound to the NH group of **1** provided greater catalyst activity than the methyl substituent. The hydrido(amine)–Ir complexes with the metal/NH bifunctional unit (**2a** and **2b**) also afforded the oxidation product acetophenone (Table 2, entries 3 and 4), whereas hydrido complex **2c**, which bears an *N*,*N*-dimethylamino group, did not exhibit catalytic activity under otherwise identical conditions (Table 2, entry 5), possibly because the aerobic dehydrogenation proceeds through the interconversion between the amine/amido catalyst intermediates. Binary catalyst systems, including the chloro(amine)–Ir complex **3** and $KOC(CH_3)_3$, were applicable to the aerobic oxidation (Table 2, entries 6 and 7). Although the chloro(amine)–Rh complexes **4** in combination with $KOC(CH_3)_3$ (Table 2, entries 8 and 9) allowed comparable catalyst performance, the related Ru systems gave unsatisfactory results, possibly due to facile decomposition in the presence of O_2 (Table 2, entries 10 and 11).



Other secondary alcohols were converted into the corresponding ketones by using the amido–Ir complex **1a** (Table 3). The reaction of 1-phenylethanols with substituents on the arene ring afforded the acetophenone derivatives in 45–64% yield under the standard conditions (Table 3, entries 1–3). Sterically congested diphenylmethanol was also catalytically dehydrogenated to give benzophenone in 62% yield (Table 3, entry 4). The aliphatic secondary alcohol in Table 3, entry 5 was found to be a good substrate, whereas unsaturated 2-cyclohexen-1-ol gave the desired ketone product in slightly lower yield (Table 3, entry 6). Although α-hydroxy carbonyl compounds gave poor results (Table 3, entries 7 and 8), selective formation of α-hydroxyketones were accomplished by the reaction of 1,2-diols such as hydrobenzoin and 1,2-cyclohexanediol (Table 3, entries 9 and 10).

Table 2. Aerobic oxidation of 1-phenylethanol with bifunctional catalysts **1**–**5**.[a]

Entry	Catalyst	Yield [%][b]
1	[Cp*Ir{κ^2(*N*,*C*)-($NHC(C_6H_5)_2$-2-C_6H_4)}] (**1a**)	72
2	[Cp*Ir{κ^2(*N*,*C*)-($NHC(CH_3)_2$-2-C_6H_4)}] (**1b**)	66
3[c]	[Cp*IrH{κ^2(*N*,*C*)-($NH_2C(C_6H_5)_2$-2-C_6H_4)}] (**2a**)	63
4[c]	[Cp*IrH{κ^2(*N*,*C*)-($NH_2C(CH_3)_2$-2-C_6H_4)}] (**2b**)	51
5[c]	[Cp*IrH{κ^2(*N*,*C*)-($N(CH_3)_2CH_2$-2-C_6H_4)}] (**2c**)	5
6[c]	[Cp*IrCl{κ^2(*N*,*C*)-($NH_2C(C_6H_5)_2$-2-C_6H_4)}] (**3a**)	83
7[c]	[Cp*IrCl{κ^2(*N*,*C*)-($NH_2C(CH_3)_2$-2-C_6H_4)}] (**3b**)	63
8[c]	[Cp*RhCl{κ^2(*N*,*C*)-($NH_2C(C_6H_5)_2$-2-C_6H_4)}] (**4a**)	72
9[c]	[Cp*RhCl{κ^2(*N*,*C*)-($NH_2C(CH_3)_2$-2-C_6H_4)}] (**4b**)	60
10[c]	[RuCl{κ^2(*N*,*C*)-($NH_2C(C_6H_5)_2$-2-C_6H_4)}(*p*-cymene)] (**5a**)	42
11[c]	[RuCl{κ^2(*N*,*C*)-($NH_2C(CH_3)_2$-2-C_6H_4)}(*p*-cymene)] (**5b**)	39

[a] Reaction conditions: catalyst (0.10 mmol), 1-phenylethanol (1.0 mmol), THF (1 mL), air (0.1 MPa), 30°C, 3 h. [b] Yield determined by GC. [c] $KOC(CH_3)_3$ (0.1 mmol) was added.

Table 3. Aerobic oxidation of secondary alcohols with **1a**.[a]

Entry	Substrate	Product	Yield [%][b]
1	$C_6H_5CH(OH)CH_3$	$C_6H_5COCH_3$	64
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
6	2-cyclohexen-1-ol	2-cyclohexen-1-one	47
7	$C_6H_5CH(OH)COC_6H_5$	$C_6H_5COCOC_6H_5$	10
8	$C_6H_5CH(OH)CO_2CH_3$		0
9	$C_6H_5CH(OH)CH(OH)C_6H_5$	$C_6H_5COCH(OH)C_6H_5$	34
10[c]	*trans*-1,2-cyclohexanediol	2-hydroxycyclohexanone	31

[a] Reaction conditions: catalyst (0.10 mmol), alcohol (1.0 mmol), THF (1 mL), air (0.1 MPa), 30°C, 3 h. [b] Yield of isolated product. [c] 6 h.

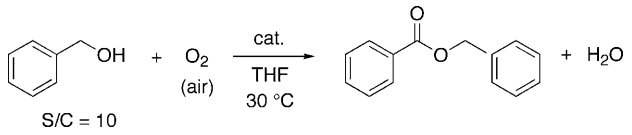
Aerobic Oxidation of Primary Alcohols

Stimulated by the promising results on the aerobic oxidation of secondary alcohols with the bifunctional Ir and Rh catalysts, we next investigated the reaction with primary alcohols [Eq. (2)]. When a mixture of benzyl alcohol containing the amido–Ir complex **1a** in THF was stirred under air at 30 °C for 6 h, benzyl benzoate was obtained in 40 % yield, along with a small amount (6 %) of benzaldehyde (Table 4, entry 1). The combined catalyst of the chloro complex **3a** with an equimolar amount of $KOC(CH_3)_3$ resulted in a comparable yield of the ester (Table 4, entry 2). Use of an excess amount of the base in the oxidation with elongated reaction time facilitated the ester formation (Table 4, entry 3). The analogous combined Rh system, **4a** and $KOC(CH_3)_3$, promoted the reaction as well (Table 4, entries 4–6).

Table 4. Aerobic oxidative esterification of benzyl alcohol.[a]

Entry	Catalyst	$KOC(CH_3)_3$ [equiv]	t [h]	Yield [%][b]
1	**1a**	0	6	40
2	**3a**	1	6	48
3	**3a**	1.2	18	64
4	**4a**	1	6	25
5	**4a**	1.2	18	46
6	**4a**	1.5	6	47

[a] Reaction conditions: catalyst (0.10 mmol), alcohol (1.0 mmol), THF (1 mL), air (0.1 MPa), 30 °C. [b] Yield of isolated product.



The scope of substrates for the oxidative dimerization with **3a** as the catalyst precursor was examined with a range of primary alcohols. The results are summarized in Table 5. The oxidation of 1,2-benzenedimethanol afforded phthalide in 72 % yield by an intramolecular esterification (Table 5, entry 2).[17] Whereas the oxidation of *p*-chlorobenzyl and *p*-methylbenzyl alcohols gave good yields (Table 5, entries 3 and 4), *p*-methoxybenzyl alcohol, which has a strongly electron-donating group, was converted into *p*-methoxybenzaldehyde in 71 % yield without formation of the ester, possibly owing to lowering of the reactivity of the aldehyde by the methoxy group (Table 5, entry 5). In the oxidation of aliphatic alcohols, esters were produced in moderate yields and with good selectivities (Table 5, entries 6 and 7).

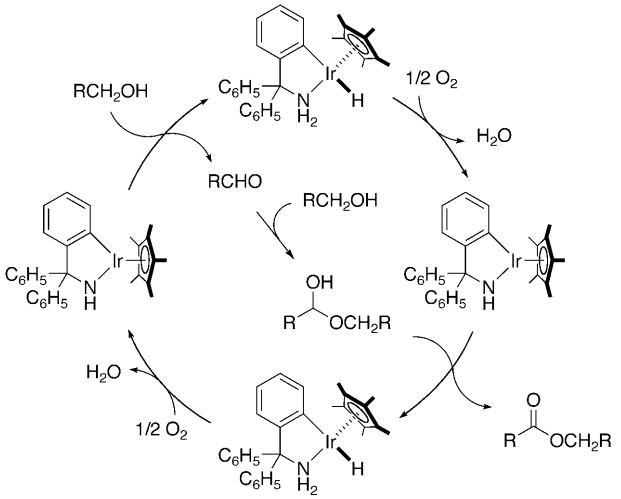
Table 5. Aerobic oxidative esterification of primary alcohols.[a]

Entry	Substrate	Product	t [h]	Yield [%][b]
1	$C_6H_5CH_2OH$	$C_6H_5CO_2CH_2C_6H_5$	18	64
2	$1,2\text{-}(HOCH_2)_2C_6H_4$	phthalide	3	72
3	$p\text{-}ClC_6H_4CH_2OH$	$p\text{-}ClC_6H_4CO_2CH_2(p\text{-}ClC_6H_4)$	3	62
4	$p\text{-}CH_3C_6H_4CH_2OH$	$p\text{-}CH_3C_6H_4CO_2CH_2(p\text{-}CH_3C_6H_4)$	18	64
5	$p\text{-}CH_3OC_6H_4CH_2OH$	$p\text{-}CH_3OC_6H_4CHO$	3	71
6	$C_6H_5CH(CH_3)CH_2OH$	$C_6H_5CH(CH_3)CO_2CH_2CH(CH_3)C_6H_5$	18	45
7	$C_6H_5(CH_2)_3OH$	$C_6H_5(CH_2)_2CO_2(CH_2)_3C_6H_5$	3	46

[a] Reaction conditions: **3a** (0.10 mmol), $KOC(CH_3)_3$ (0.12 mmol), alcohol (1.0 mmol), THF (1 mL), air (0.1 MPa), 30 °C. [b] Yield of isolated product.

Although a variety of metal catalysts have been used to promote the oxidative dimerization of primary alcohols to esters,[18–21] the reactions were conducted at high temperature except for the catalyst system of Cp*Ir(amino alcohol) complex with 2-butanone as an oxidant.[21,22] Recently, Karimi et al. reported that a unique palladium catalyst system immobilized on functionalized SBA-15 could produce esters in the aerobic oxidation of aliphatic primary alcohols.[10e] However, benzylic and allylic alcohols were not applicable to the esterification but were oxidized to the corresponding aldehydes.

To account for the dehydrogenative process with the bifunctional catalysts, a plausible mechanism is shown in Scheme 2. In the presence of O_2, the oxidation of benzyl alcohol takes place smoothly to give benzaldehyde. Subsequent attack of the remaining alcohol affords the hemiacetal, and its ready conversion into the ester is accomplished by the second oxidation.[21,22] The positive effect of using a slight excess of $KOC(CH_3)_3$ with respect to **3a** on the yield of ester is consistent with the intermediate formation of the hemiacetal.



Scheme 2. Possible reaction pathway for oxidative esterification of primary alcohols.

Conclusions

We found that a family of C–N chelate complexes bearing the metal/NH bifunctional moiety, including Ir complexes and newly synthesized Rh and Ru complexes, could facilitate the aerobic oxidation of alcohols under mild conditions of atmospheric pressure and ambient temperature, with mo-

lecular oxygen serving as an excellent hydrogen acceptor. The amido and hydrido(amine) complexes **1** and **2**, together with the combined systems of the chloro(amine) complexes **3**–**5** and $KOC(CH_3)_3$, promoted the aerobic oxidation of secondary alcohols to ketones. The reaction of primary alcohols under identical conditions afforded the oxidative dimerization product, esters, possibly via the formation of aldehydes, subsequent attack by another equivalent of alcohol to lead to hemiacetals, and successive dehydrogenation. The present work provides a new hydrogen-transfer protocol that is characterized by environmentally benign transformation as well as easy handling in laboratory procedures.

Experimental Section

General

Catalyst preparation was conducted under argon atmosphere with Schlenk techniques. Solvents were purchased from Kanto Chemical, dried by heating under reflux over sodium benzophenone ketyl (THF, toluene) or P_2O_5 (dichloromethane, hexane, acetonitrile), and distilled under argon. The catalyst precursors $[Cp^*RhCl(\mu\text{-}Cl)]_2$[23] and $[RuCl(\mu\text{-}Cl)(p\text{-cymene})]$[24] were prepared according to the literature. The synthesis of the C–N chelate Ir complexes $[Cp^*Ir\{\kappa^2(N,C)\text{-}(NHC(C_6H_5)_2\text{-}2\text{-}C_6H_4)\}]$ (**1a**), $[Cp^*Ir\{\kappa^2(N,C)\text{-}(NHC(CH_3)_2\text{-}2\text{-}C_6H_4)\}]$ (**1b**), $[Cp^*IrH\{\kappa^2(N,C)\text{-}(NH_2C(C_6H_5)_2\text{-}2\text{-}C_6H_4)\}]$ (**2a**), $[Cp^*IrH\{\kappa^2(N,C)\text{-}(NH_2C(CH_3)_2\text{-}2\text{-}C_6H_4)\}]$ (**2b**), $[Cp^*IrH\{\kappa^2(N,C)\text{-}(N(CH_3)_2CH_2\text{-}2\text{-}C_6H_4)\}]$ (**2c**), $[Cp^*IrCl\{\kappa^2(N,C)\text{-}(NH_2C(C_6H_5)_2\text{-}2\text{-}C_6H_4)\}]$ (**3a**), and $[Cp^*IrCl\{\kappa^2(N,C)\text{-}(NH_2C(CH_3)_2\text{-}2\text{-}C_6H_4)\}]$ (**3b**) was presented in our previous paper.[3] Other reagents were used as delivered. ^1H and ^{13}C NMR spectra were acquired on JEOL JNM-LA300 and JNM-ECA400 spectrometers. NMR chemical shifts were referenced to either residual proton impurities in the deuterated solvent (^1H) or the deuterated solvent (^{13}C). IR spectra were recorded on a Jasco FT/IR-610 spectrometer. Elemental analysis was carried out on a PE2400 Series II CHNS/O Analyzer (Perkin Elmer). Analytical gas chromatography was performed with a Shimadzu GC-17A gas chromatograph equipped with a DB-1 capillary column (0.25 mm × 30 m) purchased from Agilent Technologies.

Syntheses

4a: A mixture of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ (0.10 g, 0.15 mmol), tritylamine (0.31 mmol), and sodium acetate (0.032 g, 0.39 mmol) in THF (10 mL) was stirred at room temperature for 20 h. The solvent was removed under reduced pressure. After the reaction mixture was dissolved in toluene and filtered through filter paper, evaporation of the filtrate to dryness gave the rhodacycle product $[Cp^*RhCl\{\kappa^2(N,C)\text{-}(NH_2C(C_6H_5)_2\text{-}2\text{-}C_6H_4)\}]$ (**4a**). Orange crystals (0.14 g, 0.27 mmol, 89%) suitable for X-ray crystallography were obtained by slow diffusion of hexane into a solution of **4a** in CH_2Cl_2. IR (KBr): $\tilde{\nu}$ = 3292 (m), 3229 (m), 3038 (w), 2911 (w), 1584 (m), 1571 (m), 1443 (m), 1023 (m), 765 (m), 750 (m), 732 cm^{-1} (m); ^1H NMR (399.8 MHz, CD_2Cl_2, RT): δ = 1.38 (s, 15H; $C(CH_3)_5$), 4.19, 5.25 (2 × d, $^2J_{H,H}$ = 10.0 Hz, 1H; $NH_2C(C_6H_5)_2C_6H_4$), 6.83–7.43 ppm (m, 14H; $NH_2C(C_6H_5)_2C_6H_4$); $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2, RT): δ = 9.1 ($C_5(CH_3)_5$), 77.9 ($NH_2C(C_6H_5)_2C_6H_4$), 95.0 (d, $^1J_{C,Rh}$ = 6.7 Hz; $C_5(CH_3)_5$), 122.4, 127.1, 127.4, 127.6, 128.5, 128.6, 128.7, 128.9, 129.1, 137.2, 145.1, 148.4, 153.5, 171.0 ppm (d, $^1J_{C,Rh}$ = 30.7 Hz; $NH_2C(C_6H_5)_2C_6H_4$); elemental analysis: calcd (%) for $C_{29}H_{31}NClRh(CH_2Cl_2)_{0.1}$: C 64.68, H 5.82, N 2.59; found: C 64.31, H 5.83, N 2.49.

4b: A mixture of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ (0.10 g, 0.15 mmol), cumylamine (0.31 mmol), and sodium acetate (0.032 g, 0.39 mmol) in THF (10 mL) was stirred at room temperature for 20 h. The solvent was removed under reduced pressure. After the reaction mixture was dissolved in toluene and filtered through filter paper, evaporation of the filtrate to dryness gave the rhodacycle product $[Cp^*RhCl\{\kappa^2(N,C)\text{-}(NH_2C(CH_3)_2\text{-}2\text{-}C_6H_4)\}]$ (**4b**). Red crystals (0.12 g, 0.30 mmol, 99%) suitable for X-ray crystallography were obtained by slow diffusion of hexane into a solution of **4b** in toluene. ^1H NMR (399.8 MHz, CD_2Cl_2, RT): δ = 1.57, 1.62 (2 × s, 3H; $NH_2C(CH_3)_2C_6H_4$), 1.66 (s, 15H; $C(CH_3)_5$), 3.09, 3.93 (2 × br s, 1H; $NH_2C(CH_3)_2C_6H_4$), 6.71–6.73, 6.87–6.91, 6.98–7.02, 7.43–7.45 ppm (4 × m, 1H; $NH_2C(CH_3)_2C_6H_4$); $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2, RT): δ = 9.4 ($C_5(CH_3)_5$), 30.8, 32.3 ($NH_2C(CH_3)_2C_6H_4$), 64.5 ($NH_2C(CH_3)_2C_6H_4$), 94.6 (d, $^1J_{C,Rh}$ = 6.7 Hz; $C_5(CH_3)_5$,), 121.4, 124.8, 128.5, 136.8, 155.2, 167.5 ppm (d, $^1J_{C,Rh}$ = 29.7 Hz; $NH_2C(CH_3)_2C_6H_4$); elemental analysis: calcd (%) for $C_{19}H_{27}NClRh$: C 55.96, H 6.67, N 3.43; found: C 56.08, H 6.72, N 3.36.

5a: A mixture of $[RuCl(\mu\text{-}Cl)(p\text{-cymene})]_2$ (0.10 g, 0.16 mmol), tritylamine (0.33 mmol), and sodium acetate (0.033 g, 0.40 mmol) in CH_3CN (10 mL) was stirred at 60°C for 20 h. The solvent was removed under reduced pressure. After the reaction mixture was dissolved in toluene and filtered through filter paper, evaporation of the filtrate to dryness gave the ruthenacycle product $[RuCl\{\kappa^2(N,C)\text{-}(NH_2C(C_6H_5)_2\text{-}2\text{-}C_6H_4)\}(p\text{-cymene})]$ (**5a**; 0.11 g, 0.20 mmol, 61%). IR (KBr): $\tilde{\nu}$ = 3265 (m), 3230 (m), 3052 (m), 2965 (m), 1595 (m), 1571 (m), 1442 (m), 1036 (w), 1220 (w), 771 (w), 761 (m), 747 cm^{-1} (m); ^1H NMR (399.8 MHz, CD_2Cl_2, RT): δ = 1.19, 1.23 (2xd, $^3J_{H,H}$ = 6.9 Hz, 3H, $CH_3C_6H_4CH(CH_3)_2$), 1.57 (s, 3H; $CH_3C_6H_4CH(CH_3)_2$), 2.64 (tt, $^3J_{H,H}$ = 6.9, 6.9 Hz, 1H, $CH_3C_6H_4CH(CH_3)_2$), 3.50, 4.80 (2 × br s, 1H; $C(C_6H_5)_2NH_2$), 4.93, 4.99, 5.41, 6.12 (4 × d, $^3J_{H,H}$ = 5.4 Hz, 1H, $CH_3C_6H_4CH(CH_3)_2$), 6.14 (d, $^3J_{H,H}$ = 6.1 Hz, 1H; $C_6H_4C(C_6H_5)_2NH_2$), 6.70–6.72 (m, 1H, $C_6H_4C(C_6H_5)_2NH_2$), 6.93–7.45 (11H, $C_6H_4C(C_6H_5)_2NH_2$), 7.87 ppm (d, $^3J_{H,H}$ = 7.3 Hz, $C_6H_4C(C_6H_5)_2NH_2$); $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2, RT): δ = 18.0 ($CH_3C_6H_4C(CH_3)_2$), 21.4, 23.8 ($CH_3C_6H_4C(CH_3)_2$), 30.9 ($CH_3C_6H_4C(CH_3)_2$), 73.0 ($NH_2C(C_6H_5)_2C_6H_4$), 75.7, 78.3, 80.6, 85.5, 95.8, 109.2 ($CH_3C_6H_4CH(CH_3)_2$), 121.8, 126.3, 126.7, 127.4, 128.0, 128.2, 128.3, 128.7, 138.6, 138.4, 144.2, 147.1, 150.4, 151.9 ppm ($C_6H_4C(C_6H_5)_2NH_2$); elemental analysis: calcd (%) for $C_{29}H_{30}NClRu$: C 65.83, H 5.72, N 2.65; found: C 65.90, H 5.74, N 2.64.

5b: A mixture of $[RuCl(\mu\text{-}Cl)(p\text{-cymene})]_2$ (0.10 g, 0.16 mmol), cumylamine (0.33 mmol), and sodium acetate (0.033 g, 0.40 mmol) in CH_3CN (10 mL) was stirred at 60°C for 20 h. The solvent was removed under reduced pressure. After the reaction mixture was dissolved in toluene and filtered through filter paper, evaporation of the filtrate to dryness gave the ruthenacycle product $[RuCl\{\kappa^2(N,C)\text{-}(NH_2C(CH_3)_2\text{-}2\text{-}C_6H_4)\}(p\text{-cymene})]$ (**5b**; 0.058 g, 0.14 mmol, 45%). ^1H NMR (300.4 MHz, CD_2Cl_2, RT): δ = 1.18 (s, 3H, $C(CH_3)_2NH_2$), 1.22, 1.25 (2xd, $^3J_{H,H}$ = 6.8 Hz, 3H, $CH_3C_6H_4CH(CH_3)_2$), 1.55 (s, 3H; $C(CH_3)_2NH_2$), 1.92 (s, 3H; $CH_3C_6H_4CH(CH_3)_2$), 2.80 (tt, $^3J_{H,H}$ = 6.8, 6.8 Hz, 1H; $CH_3C_6H_4CH(CH_3)_2$), 3.86, 3.93 (2 × br s, 1H, $C(CH_3)_2NH_2$), 4.77, 5.06, 5.13, 5.48 (4 × d, $^3J_{H,H}$ = 5.6 Hz, 1H, $CH_3C_6H_4CH(CH_3)_2$), 6.68–6.71, 6.84–6.89, 7.18–7.24, 7.78–7.81 ppm (4 × m, 1H, $NH_2C(CH_3)_2C_6H_4$); $^{13}C\{^1H\}$ NMR (75.6 MHz, CD_2Cl_2, RT): δ = 18.5 ($CH_3C_6H_4CH(CH_3)_2$), 21.5, 23.9 ($CH_3C_6H_4CH(CH_3)_2$), 31.3 ($CH_3C_6H_4CH(CH_3)_2$), 31.4, 31.9 ($C_6H_4C(CH_3)_2NH_2$), 54.5 ($C_6H_4C(CH_3)_2NH_2$), 65.0, 78.0, 82.7, 84.0, 86.2, 108.9 ($CH_3C_6H_4CH(CH_3)_2$), 121.5, 122.7, 126.6, 139.6, 152.7 ppm ($C_6H_4C(CH_3)_2NH_2$); elemental analysis: calcd (%) for $C_{19}H_{26}NClRu(C_6H_5CH_3)_{0.25}$: C 58.23, H 6.59, N 3.27; found: C 58.56, H 6.65, N 3.15.

Aerobic oxidation of 1-phenylethanol catalyzed by Ir, Rh, or Ru complexes **1**–**5**: A 20-mL Schlenk flask was charged with the respective catalyst (0.10 mmol), durene (0.024 mg, 1.1 mmol; an internal standard), and THF (1.0 mL) under Ar atmosphere. When the chloro complex **3**, **4**, or **5** was used as the catalyst precursor, $KOC(CH_3)_3$ (0.10 mmol) was added to the catalyst solution. After 1-phenylethanol (1.0 mmol) had been introduced, the flask was filled with air. The reactions were carried out at 30°C under an air balloon for 3 h. After the removal of the metal catalyst from the reaction mixture by filtration through a short plug of silica, the product acetophenone was analyzed by GC.

Aerobic oxidation of secondary alcohols catalyzed by amido–Ir complex **1a**: In a 20-mL Schlenk flask, the appropriate secondary alcohol (1.0 mmol) was added to a solution of **1a** (0.10 mmol) in THF (1.0 mL), and the flask was then filled with air. The reaction was carried out at 30°C under an air balloon for 3 h. The crude products were purified by column chromatography on silica gel. The products were characterized by comparison with data of authentic samples (NMR, TLC).

Aerobic oxidative condensation of primary alcohols: A 20-mL Schlenk flask was charged with the respective catalyst (0.10 mmol) and THF (1.0 mL) under Ar atmosphere. When the chloro complex **3** or **4** was used as the catalyst precursor, $KOC(CH_3)_3$ (0.10–0.15 mmol) was added to the catalyst solution. After the appropriate primary alcohol (1.0 mmol) had been introduced, the flask was filled with air. The reaction mixture was stirred at 30 °C under an air balloon. The crude products were purified by column chromatography on silica gel. The products were characterized by comparison with data of authentic samples (NMR, TLC).

*X-ray Structure Determination of **4a** and **4b***

All measurements were made on a Rigaku Saturn CCD area detector equipped with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) under a nitrogen stream at 193 K. Indexing was performed from seven images. The crystal-to-detector distance was 45.05 mm. Data were collected to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected. A sweep of data was carried out by using ω scans from −110.0 to 70.0° in 0.5° steps at $\chi = 45.0°$ and $\phi = 0.0°$. A second sweep was performed by using ω scans from −110.0 to 70.0° in 0.5° steps at $\chi = 45.0°$ and $\phi = 90.0°$. Intensity data were collected for Lorentz-polarization effects as well as absorption. Structure solution and refinement were performed with the CrystalStructure program package. Heavy-atom positions were determined by a direct-program method (SIR2002), and the remaining non-hydrogen atoms were found by subsequent Fourier techniques (DIRDIF99). An empirical absorption correction based on equivalent reflections was applied to all data. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques based on F^2. All hydrogen atoms were constrained to ride on their parent atom. Relevant crystallographic data are compiled in Table 1.

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