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Catalytic Behavior of Cationic Hydridoruthenium(II) Complex, $[RuH(NH_3)(PMe_3)_4]^+$, in H_2-Hydrogenation and Transfer Hydrogenation of Imines

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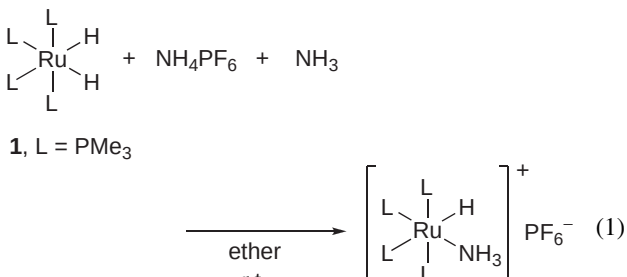
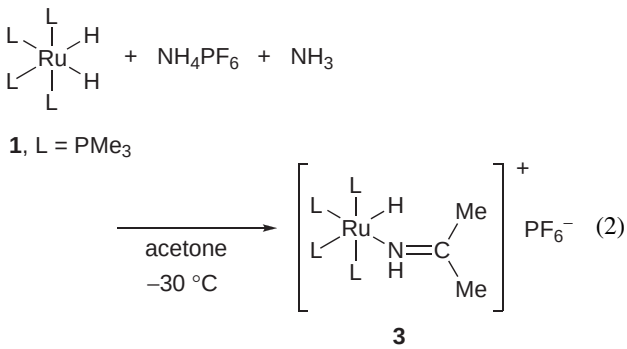
Catalytic hydrogenation under H_2 and transfer hydrogenation of imines by secondary alcohols with hydridoruthenium complexes bearing PMe_3 and PPh_3 ligands have been examined. A cationic hydridoruthenium complex, *cis*-$[RuH(NH_3)(PMe_3)_4]PF_6$ (**2**), derived from *cis*-$[RuH_2(PMe_3)_4]$ (**1**) and NH_4PF_6, showed higher catalytic activity for H_2-hydrogenation of *N*-benzylideneaniline than neutral complexes such as **1** and *cis*-$[RuClH(PMe_3)_4]$ (**6**). The effectiveness of cationic hydridoruthenium species for the catalytic H_2-hydrogenation of benzylideneaniline was also demonstrated by a marked increase in the yield of *N*-benzylaniline on treatment of **6** with $AgPF_6$. The cationic complex **2** was applicable to catalytic transfer hydrogenation of imines with secondary alcohols even in the absence of a base. Isotope labeling experiments using deuterated alcohols revealed that the hydrogen atom bound to the α-carbon of the donor alcohol was transferred exclusively to the imine carbon and alcoholic OD was transferred to the imine nitrogen. A rapid exchange between the alcoholic proton and the hydrido ligand of **2** was also confirmed by NMR investigation using $(CH_3)_2CHOD$. On the basis of the experimental results the mechanisms of the H_2-hydrogenation and transfer hydrogenation are discussed.

The reduction of imines to amines is a convenient transformation for synthesizing amines as useful building blocks in pharmaceuticals and agrochemicals. A large body of work has been devoted over the past decades to designing effective transition-metal complexes for catalytic hydrogenation and transfer hydrogenation of imines.[1] In these processes, catalytic cycles involving formation of metal hydrides and the subsequent hydrogen transfer to activated imines have been widely assumed.[2] We have previously reported the synthesis and some catalytic activities of cationic monohydridoruthenium complexes bearing trimethylphosphine.[3] While a cationic complex, *cis*-$[RuH(NH_3)(PMe_3)_4]PF_6$ (**2**), can be easily prepared by treatment of a neutral dihydrido complex, *cis*-$[RuH_2(PMe_3)_4]$ (**1**), with an equimolar amount of NH_4PF_6 in the presence of NH_3 in diethyl ether, use of acetone yielded an isopropylideneamine-coordinated hydridoruthenium complex *cis*-$[RuH(HN{=}CMe_2)(PMe_3)_4]PF_6$ (**3**) (eqs 1 and 2). When the protonolysis of **1** with NH_4PF_6 was performed in a hydrogen atmosphere at $-60\,^{\circ}C$ under otherwise identical conditions to the formation of **3**, an amine-coordinated hydridoruthenium complex *cis*-$[RuH(H_2NCHMe_2)(PMe_3)_4]PF_6$ (**4**) was obtained via hydrogenation of isopropylideneamine (eq 3). These cationic hydrido complexes **3** and **4** can be regarded as models of the intermediates active in the catalytic hydrogenation of imines to amines.





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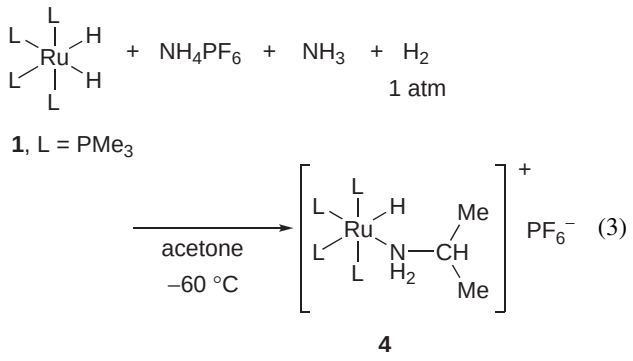

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In the course of our studies on cationic group 10 metal complexes, it has been found that creation of a coordination site available for incoming reaction components by removal of a halogen ligand in neutral alkyl and acyl halide complexes with silver salts gives rise to promotion of β-hydrogen elimination, olefin and CO insertion, and nucleophilic attack on coordinating CO.[4–8] Since the cationic hydridoruthenium complexes with hemilabile N-donor groups such as **2**–**4** are also expected to provide an appropriate reaction environment for reduction of imines, we have extended the work to evaluate the catalyst behavior of a series of hydridoruthenium complexes. Here, we wish to present our results demonstrating the marked increase in the catalytic activities of hydridoruthenium complexes in the H_2-hydrogenation and transfer hydrogenation of imines with secondary alcohols by generating a cationic active center from neutral species. We also examined the transfer hydrogenation mechanism using deuterium-labeled compounds, and propose a catalytic cycle operating through a ruthenium-catalyzed hydrogen-transfer process on the basis of fundamental studies of the model ruthenium complexes.

Results and Discussion

Hydrogenation of Imines Catalyzed by Cationic Hydridoruthenium Complexes under Dihydrogen. The catalytic activity of a cationic hydridoruthenium complex, *cis*-[RuH(NH$_3$)(PMe$_3$)$_4$]PF$_6$ (**2**), in the hydrogenation of *N*-benzylideneaniline under hydrogen (to be referred hereafter as H_2-hydrogenation) was tested first (eq 4). Table 1 shows the effects of hydrogen pressure, reaction temperature, and solvent on the H_2-hydrogenation of *N*-benzylideneaniline performed in a substrate/catalyst ratio of 60. Increasing the hydrogen pressure led to increase of the hydrogenation yield (Entries 1–3), with best results obtained in the reaction with 65 atm of H_2 at 80 °C in THF for 15 h to give *N*-benzylaniline in 95% yield. The reaction time could be reduced to 6 h under otherwise identical conditions without severely affecting the yield (Entry 4), while the H_2-hydrogenation was strongly retarded by decreasing the temperature (Entries 5 and 6). The hydrogenation also proceeded efficiently in 1,4-dioxane (Entry 7), but the product yield dropped sharply in Et$_2$O, possibly due to poor solubility of the cationic complex **2** in Et$_2$O (Entry 8). Decrease in the catalytic activity was observed by using other solvents with higher coordinating ability (Entries 10–12).

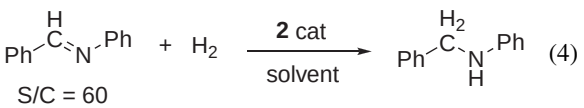

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Table 1. Catalytic Hydrogenation of *N*-Benzylideneaniline by the Cationic Complex **2** under Hydrogen Pressure[a]

Entry	Pressure/atm	Time/h	Temp/°C	Solvent	Yield/%[b]
1	10	15	80	THF	56
2	30	15	80	THF	70
3	65	15	80	THF	95
4	65	6	80	THF	88
5	65	6	50	THF	50
6	65	6	rt	THF	3
7	65	6	80	dioxane	86
8	65	6	80	Et_2O	4
9	65	6	80	CH_2Cl_2	75
10	65	6	80	acetone	58
11	65	6	80	MeOH	30
12	65	6	80	CH_3CN	1

a) Reaction conditions: **2** (0.02 mmol), imine (1.2 mmol), solvent (13 mL). b) GC yield.

Table 2. Hydrogenation of *N*-Benzylideneaniline with Ru Catalysts under Hydrogen Pressure[a]

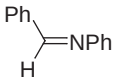
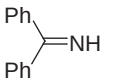
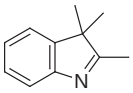
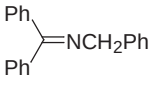
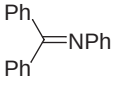
Entry	Ru catalyst	Yield/%[b]
1	*cis*-[RuH$_2$(PMe$_3$)$_4$] (**1**)	33
2	*cis*-[RuH(NH$_3$)(PMe$_3$)$_4$]PF$_6$ (**2**)	88
3	[RuH(PMe$_3$)$_5$]PF$_6$ (**5**)	61
4	*cis*-[Ru(NH$_3$)$_2$(PMe$_3$)$_4$][PF$_6$]$_2$	75
5	*cis*-[RuClH(PMe$_3$)$_4$] (**6**)	1
6	**6** + AgPF$_6$ (1 mol amt.)	83
7	*cis*-[RuH$_2$(PPh$_3$)$_4$] (**7**)	20
8	**7** + NH$_4$PF$_6$ (1 mol amt.)	66

a) Reaction conditions: Ru cat (0.02 mmol), imine (1.2 mmol), THF, 65 atm, 80 °C, 6 h. b) GC yield.

The nature of the catalyst strongly affected the outcome of the catalytic H_2-hydrogenation as summarized in Table 2. It is noted that the cationic monohydrido complex **2** having four PMe$_3$ ligands showed a greater activity toward the H_2-hydrogenation than the neutral dihydrido complex **1** having the same number of PMe$_3$ ligands (Entries 1 and 2). Replacement of the NH$_3$ ligand in **2** with more strongly coordinating PMe$_3$ resulted in decrease of the yield from 88% to 61%, indicating that the availability of a coordination site for the incoming substrate is important in the catalysis (Entry 3).[9] A dicationic ruthenium complex, *cis*-[Ru(NH$_3$)$_2$(PMe$_3$)$_4$][PF$_6$]$_2$ prepared from **1** by treatment with 2 mol equiv of NH$_4$PF$_6$, can also hydrogenate the imine (Entry 4). Although a neutral monohydrido complex, *cis*-[RuClH(PMe$_3$)$_4$] (**6**) proved to be an inactive catalyst precursor, H_2-hydrogenation in the presence of AgPF$_6$, which is used to abstract the chloride ligand from **6**, gave the hydrogenation product in a yield of 83%, which is comparable to the result found for cationic monohydrido complex **2** (Entries 5, 6, and 1). The promoting effect of generating a cationic species in this process was also observed for Ru–PPh$_3$ systems. While a neutral dihydridoruthenium complex, [RuH$_2$(PPh$_3$)$_4$] (**7**), afforded the hydrogenation product in only 20% yield, the in situ generation of a cationic monohydrido complex by treatment of **7** with 1 mol equiv of NH$_4$PF$_6$ led to increase of the yield to 66% (Entries 7 and 8).

Next we examined the effects of reaction conditions for H_2-

Table 3. Hydrogenation of Imines with the Cationic Complex **2** under Hydrogen Pressure[a)]

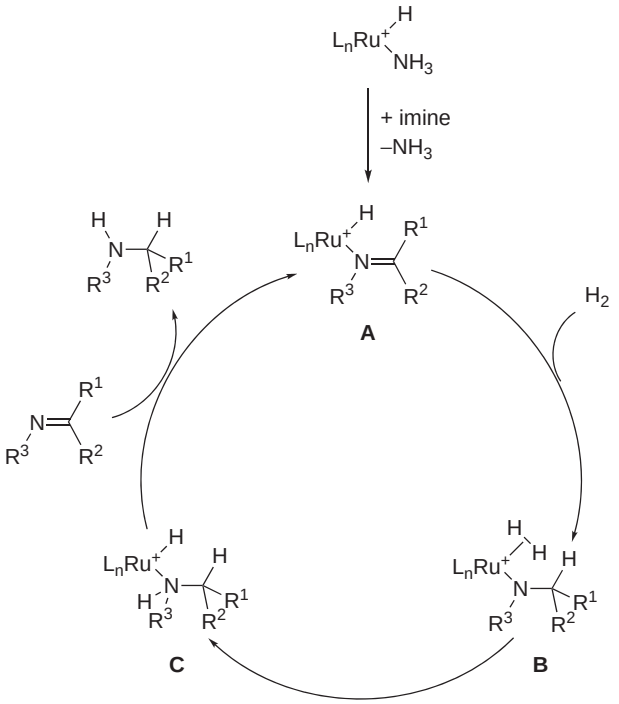
Entry	Substrate	Pressure/atm	Time/h	Yield/%[b)]
1		65	15	95
2		65	14	90
3		85	49	99
4		65	168	50
5		65	168	10

a) Reaction conditions: Ru cat (0.02 mmol), imine (1.2 mmol), THF, 80 °C. b) GC yield.

hydrogenation of various imines by using the cationic hydridoruthenium complex **2** having four PMe_3 ligands. Table 3 shows that *N*-benzylideneaniline was hydrogenated under hydrogen pressure of 65 atm at 80 °C to give *N*-benzylaniline in 95% yield after 15 h (Entry 1). Diphenylmethyleneimine also afforded the corresponding amine in 90% yield under the standard conditions of a substrate/catalyst ratio of 60 and H_2 pressure of 65 atm at 80 °C (Entry 2). Tri-substituted imines were also found to be catalytically hydrogenated albeit slowly. The H_2-hydrogenation of 2,3,3-trimethylindolenine required higher pressure of 85 atm with a prolonged reaction time of 49 h (Entry 3). The use of more sterically congested diphenylmethyleneimines resulted in incomplete reaction (Entries 4 and 5).

On the basis of experimental results concerning the behavior of neutral and cationic hydridoruthenium complexes,[3a] we propose a catalytic cycle for H_2-hydrogenation of imines by a cationic ruthenium complex as depicted in Scheme 1. Since the cationic imine-coordinated hydridoruthenium complex **3** can be obtained by treatment of **1** with NH_4PF_6 under NH_3 in acetone (eq 2), it is reasonable to assume the formation of an analogous hydridoruthenium complex **A** as the first step in the catalytic cycle. Under hydrogen pressure, insertion of the coordinated imine into the Ru–H bond takes place to give an H_2-bound amidoruthenium complex **B**. The proton transfer from the η^2-bound H_2 onto the amide nitrogen in **B** gives a hydridoruthenium complex coordinated with the amine, **C**, corresponding to the isolated complex **4** (eq 3).[10] Replacement of the coordinated amine ligand in **C** with the substrate imine liberates the product amine, regenerating **A**, which carries the catalytic cycle further. The experimental results obtained for the PMe_3-coordinated complexes **1** to **4** (eqs 1–4) lend support to the credibility of operation of the H_2-hydrogenation mechanism as shown in Scheme 1.

Transfer Hydrogenation of *N*-Benzylideneaniline with Secondary Alcohols Catalyzed by Hydridoruthenium Complexes. Stimulated by the observation of a marked promoting



Scheme 1.

effect by conversion of the neutral complexes into the cationic hydridoruthenium species in the imine hydrogenation under H_2, we next investigated transfer hydrogenation of imines with 2-propanol as an alternative hydrogenation process, which can be performed experimentally more conveniently without using an autoclave. Since the $[Ru_3(CO)_{12}]$-catalyzed reaction was reported first by Jones' group,[11] several ruthenium complexes have been tested for transfer hydrogenation of imines with 2-propanol.[12–18] Wang and Bäckvall reported that a Ru–PPh_3 complex, $[RuCl_2(PPh_3)_3]$, catalyzes transfer hydrogenation of imines with 2-propanol and that addition of K_2CO_3 dramatically enhances the catalytic activity of the ruthenium complex.[12] The role of the base was ascribed to formation of an alkoxoruthenium species that undergoes further β-H elimination to produce a cationic ruthenium hydride species.[19] On the other hand, Yamagishi and co-workers demonstrated that a neutral dihydrido complex, *cis*-$[RuH_2(PPh_3)_4]$ (**7**), showed a high catalytic activity for the transfer hydrogenation reaction of imines even in the absence of a base, whereas a neutral monohydrido complex, *cis*-$[RuClH(PPh_3)_3]$ (**8**), required the addition of KOH to generate an active dihydridoruthenium intermediate, *cis*-$[RuH_2(PPh_3)_n]$.[13]

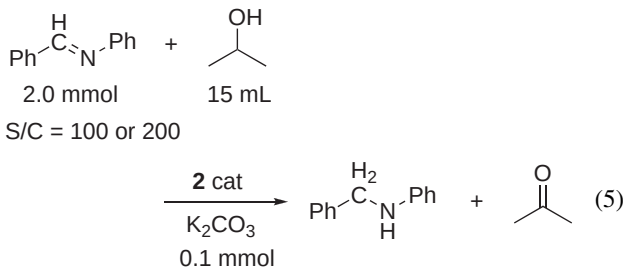
We examined the catalytic activity of the cationic monohydridoruthenium complex, *cis*-$[RuH(NH_3)(PMe_3)_4]PF_6$ (**2**), for the transfer hydrogenation of *N*-benzylideneaniline in 2-propanol in the presence of K_2CO_3 as a base (eq 5) and obtained results as listed in Table 4. When the reaction was performed with a substrate:base:catalyst ratio of 100:5:1, *N*-benzylaniline was obtained in a yield of 92% after refluxing the catalytic system for 13 h (Entry 1). An almost quantitative yield was achieved by further elongation of the reaction time to 24 h (Entry 2). The catalyst loading can be reduced to a substrate/catalyst ratio of 200 (Entry 3), whereas lowering the reaction temperature to 50 °C caused a sharp decrease in the

Table 4. Transfer Hydrogenation of *N*-Benzylideneaniline with 2-Propanol by Ru Complexes in the Presence of K_2CO_3[a)]

Entry	Ru cat	Imine/Ru cat	Time/h	Yield/%[b)]
1	**2**	100	13	92
2	**2**	100	24	>99
3	**2**	200	16	92
4[c)]	**2**	100	24	1
5[d)]	**2**	100	12	95
6[e)]	**2**	100	5	89
7	**5**	200	24	82
8	**1**	100	18	83
9	**8**	200	22	97

a) Reaction conditions: imine (2.0 mmol), K_2CO_3 (0.1 mmol), 2-propanol (15 mL), 80 °C. b) GC yield. c) At 50 °C. d) The reaction was carried out in 2-butanol under reflux conditions at 98 °C. e) The reaction was carried out in 3-pentanol under reflux conditions at 116 °C.

yield of amine (Entry 4). The transfer hydrogenation reaction also proceeds with other secondary alcohols. *N*-benzylideneaniline was readily reduced to *N*-benzylaniline in 2-butanol and 3-pentanol as hydrogen sources under refluxing conditions (Entries 5 and 6). A yield as high as 95% was obtained in 12 h with 2-butanol and 89% yield was obtained in 5 h with 3-pentanol. The higher yields with 2-butanol and 3-pentanol than with 2-propanol are ascribable to their higher boiling temperatures than that of 2-propanol. The cationic complex, $[RuH(PMe_3)_5]PF_6$ (**5**), having five PMe_3 ligands proved somewhat less reactive than **2** (Entry 7), probably due to the presence of the strongly coordinating PMe_3 ligands occupying the available reaction site for the imine substrate. The neutral dihydridoruthenium complex **1** bearing four PMe_3 ligands also promoted the reaction in the presence of a base with a slightly lower activity than **2** (Entry 8). A monohydridoruthenium complex, *cis*-$[RuClH(PPh_3)_3]$ (**8**), catalyzed the transfer hydrogenation effectively in the presence of K_2CO_3 as well (Entry 9).



We next examined the effect of addition of a base in the Ru-catalyzed transfer hydrogenation of *N*-benzylideneaniline (Table 5). It is noted that the transfer hydrogenation of *N*-benzylideneaniline with **2** and **1** proceeded in the absence of K_2CO_3 (Entries 1–4), whereas addition of base was crucial for the catalyst activity in the case of the neutral *cis*-$[RuClH(PPh_3)_3]$ (**8**) as reported by Wang and Bäckvall[12] and Yamagishi et al.,[13] independently (Entries 5 and 6).

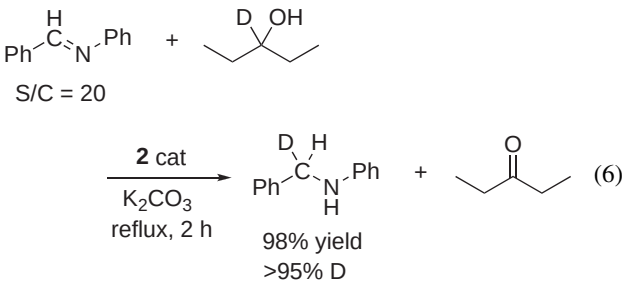
Mechanistic Considerations on Transfer Hydrogenation of Imines with Secondary Alcohols Catalyzed by the Cationic Hydridoruthenium Complex 2. In order to obtain information on the course of transfer hydrogenation of imines

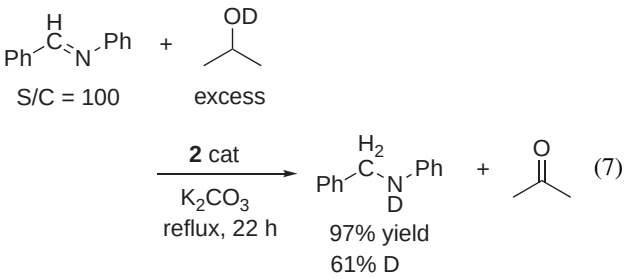
Table 5. Effect of K_2CO_3 on Transfer Hydrogenation of *N*-Benzylideneaniline with 2-Propanol[a)]

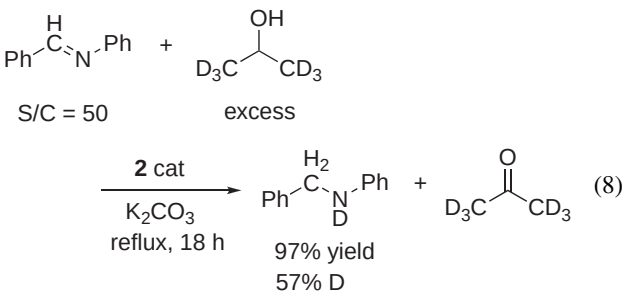
Entry	Ru cat	Imine/Ru cat	Additive	Time/h	Yield/%[b)]
1	**2**	100	K_2CO_3[c)]	13	92
2	**2**	100	—	18	66
3	**1**	100	K_2CO_3[c)]	18	83
4	**1**	100	—	21	79
5	**8**	200	K_2CO_3[c)]	22	97
6	**8**	200	—	22	0

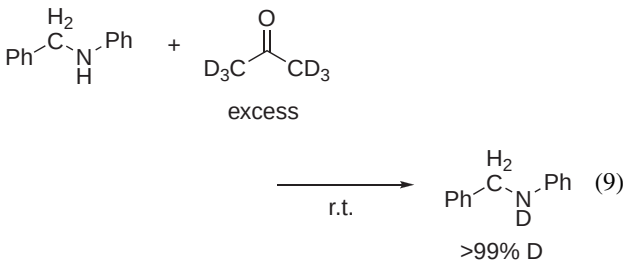
a) Reaction conditions: imine (2.0 mmol), 2-propanol (15 mL), 80 °C. b) GC yield. c) K_2CO_3/Ru cat = 5.

catalyzed by the cationic monohydrido complex **2**, we carried out deuterium-labeling experiments for the transfer hydrogenation of *N*-benzylideneaniline (eqs 6–9). When the transfer hydrogenation of *N*-benzylideneaniline was conducted in the presence of **2** in 3-pentanol-3-*d*, $(C_2H_5)_2CDOH$, under refluxing conditions for 2 h, *N*-benzylaniline was obtained in 98% yield and both ^1H and ^2H NMR spectroscopy revealed that the deuterium was cleanly transferred to the benzylidene carbon whereas the alcoholic hydrogen was transferred to the imine nitrogen giving the deuterated benzylaniline selectively as shown in eq 6. The $^{13}C\{^1H\}$ NMR spectrum of the produced amine exhibits a triplet signal of the benzylic carbon at 47.8 ppm with a $^1J_{C-D}$ coupling constant of 20.5 Hz, indicating that only one deuterium atom was incorporated into the benzylic position.









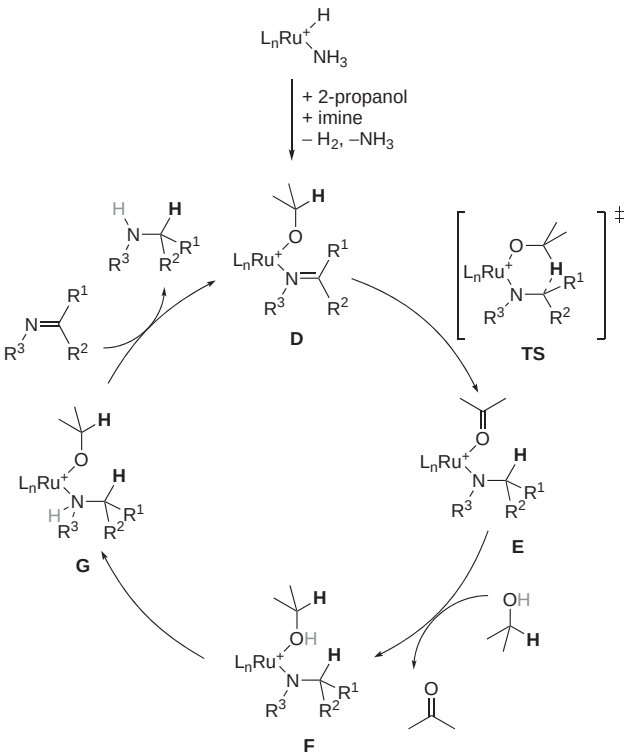
(9)

As a cross-labeling experiment, we carried out the transfer hydrogenation of *N*-benzylideneaniline with $(CH_3)_2CHOD$ (98% D content) (eq 7). In this case, no deuteration occurred on the benzylidene carbon, whereas deuteration at the nitrogen (61%) was observed. For further cross-examination of the labeling experiments in eqs 6 and 7, we carried out hydrogen-transfer reaction with $(CD_3)_2CHOH$ catalyzed by **2** (eq 8). *N*-Benzylaniline, the transfer hydrogenation product, was produced in 97% yield, and the amine proton was labeled with 57% deuteration, whereas no deuteration occurred on the benzyl carbon.

We reasoned that the lowering of the deuterium content at the amine nitrogen in eq 7 was caused by the H–D exchange of the introduced deuterium at the amine nitrogen with the enolic proton in the non-deuterated acetone produced as the co-product. In fact, occurrence of such H–D exchange was confirmed by a reference experiment, where unlabeled *N*-benzylaniline was treated in an acetone-d_6 solution without a Ru catalyst at room temperature (eq 9). The result of the reference experiment showing the 99% deuterium labeling at the amine nitrogen indicates ready occurrence of the uncatalyzed H–D exchange between *N*-benzylaniline and deuterated acetone.

The results of the deuterium-labeling experiments, shown in eqs 6–8, can be accounted for by two types of mechanisms. One is the Meerwein–Ponndorf–Verley (MPV) mechanism and the other is a mechanism involving ruthenium hydride species. A possible MPV type mechanism proceeding through a cyclic transition state (**TS**) is shown in Scheme 2. The MPV mechanism was originally proposed for the transfer hydrogenation catalysis promoted by aluminum alkoxides and there is no established example that a transition-metal complex served as the catalyst in this type of transfer hydrogenation.[20,21] However, since a hydridoruthenium complex is known to form an alkoxide on reaction with alcohols,[22] formation of a ruthenium alkoxide should take place readily and the MPV type mechanism in Scheme 2 deserves due consideration.

Scheme 2 assumes the formation of an imine-coordinated isopropoxide complex **D** by the reaction of cationic ruthenium hydride **2** with 2-propanol in the presence of imine. Hydrogen transfer from the isopropoxide to the coordinated imine carbon over a cyclic transition state (**TS**) gives an acetone-coordinated amido complex **E**. Liberation of the coordinated acetone with 2-propanol gives an amido intermediate coordinated with 2-propanol, **F**. Proton transfer from the coordinated 2-propanol to the amido nitrogen generates an amine-coordinated isopropoxide **G**. Replacement of the amine with the incoming imine liberates the hydrogenation product, reproducing **D** to carry the catalytic cycle. Thus the main feature of the proposed cat-



Scheme 2.

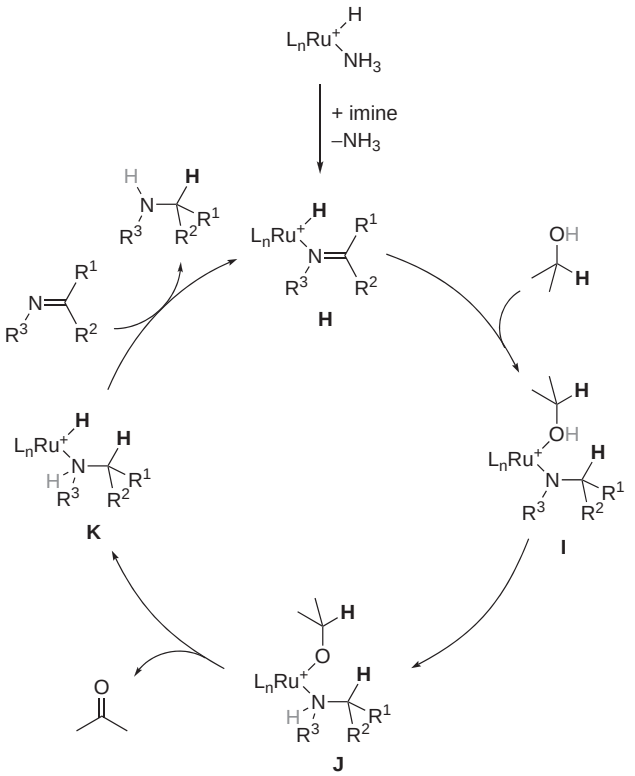
alytic cycle is similar to that of the original MPV mechanism proposed for the aluminum alkoxide catalysis, and is compatible with the experimental results obtained in the deuterium-labeling study.

However, there remain the possibilities that the transfer hydrogenation may proceed through a hydride mechanism. Scheme 3 depicts a possible catalytic cycle involving monohydrido intermediates.

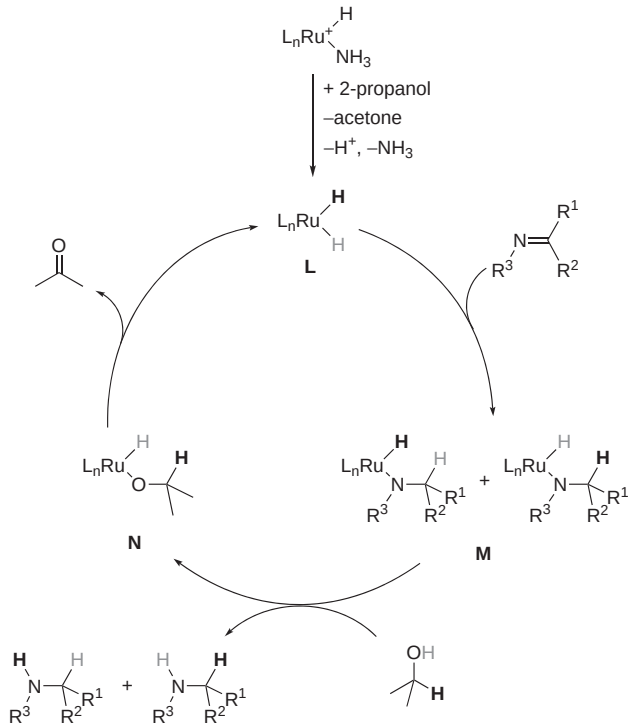
The catalytic cycle assumes participation of an imine-coordinated cationic ruthenium monohydride **H** as the starting species. The fact that we have isolated a related imine-coordinated cationic hydridoruthenium complex **3** in eq 2 supports the intermediacy of **H**. The transfer of the hydride in **H** to the coordinated imine carbon in the presence of 2-propanol forms an amido complex coordinated with 2-propanol, **I**. Proton transfer of the alcoholic OH in 2-propanol to the amide nitrogen gives an amine-coordinated isopropoxide, **J**. The subsequent β-hydrogen elimination from the isopropoxide ligand liberates acetone to afford the amine-coordinated cationic ruthenium hydride **K**. The subsequent replacement of the coordinated amine with imine would liberate the amine as the hydrogenation product and regenerate the imine-coordinated hydride complex **H**, which further carries the catalytic cycle.

The experimental results obtained in the labeling study, which showed the hydrogen transfer from the α-hydrogen in the alcohol to the imine carbon (eq 6) and the deuterium transfer from the alcoholic OD to the imine nitrogen atom to give the N-deuterated benzylaniline and acetone (eq 7) are compatible with the monohydride mechanism shown in Scheme 3.

As another possible mechanism involving ruthenium hydrides, we addressed if a catalytic cycle proceeding through



Scheme 3.

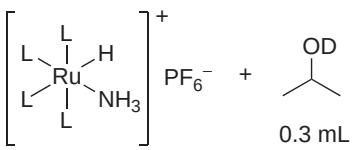


Scheme 4.

a dihydride intermediate as shown in Scheme 4 is operative. A similar catalytic cycle has been postulated based on our experimental studies on H_2-hydrogenation and transfer hydrogenation of ketones by dihydridoruthenium complexes.[23] In this mechanism the ruthenium dihydride species **L** may be generated by reaction of the monohydrido species **2** with 2-propanol through a possible formation of an isopropoxoruthenium intermediate followed by β-H elimination. The ruthenium dihydride species **L** thus produced may give an amido-hydrido species **M** by insertion of the incoming imine into one of the Ru–H bonds. Further reaction of **M** with 2-propanol would liberate the amine giving a hydrido alkoxide species **N**. The subsequent β-hydrogen elimination releases acetone to reproduce the ruthenium dihydride **L** that carries the catalytic cycle.

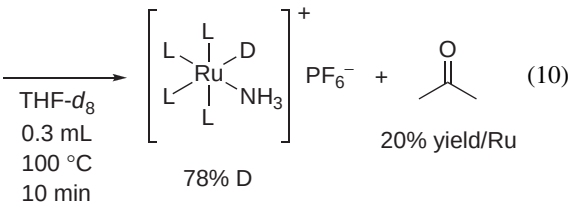
Although the dihydride mechanism shown in Scheme 4 is constituted of reasonable elementary processes, it is not compatible with the results of deuterium-labeling experiments, which showed no scrambling of the two hydrogens originated from the α-carbon and alcoholic OH (eqs 6–8). Thus the dihydride mechanism as shown in Scheme 4 may be eliminated from further consideration.[24]

A difficulty remains in choosing the MPV mechanism shown in Scheme 2 or a ruthenium monohydrido mechanism in Scheme 3. For obtaining evidence to support or disprove either of the two possibilities, we examined whether a ruthenium hydride undergoes exchange with alcoholic hydrogen or not (eq 10).[25] The experimental results showed that H–D scrambling occurred on treatment of the cationic monohydride complex **2** with $(CH_3)_2CHOD$ in THF-d_8 for 10 min at 100 °C to give the corresponding cationic ruthenium deuteride, $[RuD(PMe_3)_4(NH_3)]PF_6$, (**2**-d_1) with formation of acetone, whereas **2** was stable in the absence of added 2-propanol under otherwise identical conditions. Deuterium incorporation into the hydrido ligand with a H/D ratio of 22/78 was confirmed by the loss of intensity in the hydride resonance around −9.5 ppm in the ^{1}H NMR spectrum. The H–D scrambling was also indicated by complication of the three phosphorus signals at −15.3, −4.6, and 14.4 ppm in the $^{31}P\{^1H\}$ NMR spectrum as a result of additional P–D couplings of the phosphorus nucleus with the deuterido ligand in **2**-d_1.



2, L = PMe_3

3.0×10^{-2} mmol



(10)

The occurrence of the H–D exchange seems to be in contradiction with the involvement of a ruthenium hydride species, unless the intermediate ruthenium monohydride species has a very short lifetime for undergoing exchange with 2-propanol-d_1. The involvement of ruthenium alkoxide species **D** and **G** in Scheme 2 is supported by the experimental result of the acetone formation in eq 10, arising from β-H elimination of an isopropoxoruthenium intermediate generated from

the cationic hydrido complex **2** in 2-propanol. The available data in our hands are compatible with the MPV hydrogen-transfer mechanism proceeding through an active ruthenium alkoxide as outlined in Scheme 2.[26]

Conclusion

In this paper, we have investigated catalytic behavior of the cationic monohydridoruthenium complex *cis*-[RuH(NH_3)-(PMe_3)$_4$]PF_6 (**2**) toward H_2-hydrogenation and transfer hydrogenation of imines. Remarkable enhancement in the H_2-hydrogenation activity was observed by switching the catalyst from the neutral dihydride complex **1** to the cationic monohydride complex **2**. The addition of $AgPF_6$ to the neutral hydridoruthenium chloride complex **6** also led to enhancement of the catalytic hydrogenation activity suggesting the importance of generating an active cationic monohydride species.

The cationic hydridoruthenium complex **2** effectively catalyzed the transfer hydrogenation of *N*-benzylideneaniline by secondary alcohols. The catalytic activity of **2** was maintained even in the absence of a base, whereas basic conditions were needed for the neutral monohydride complex **8** to generate a catalytically active species. The transfer hydrogenation using deuterium-labeled alcohols by **2** revealed that no scrambling of the two hydrogens originating from the α-carbon and alcoholic oxygen of the donor alcohol occurred, and therefore the dihydride mechanism is not compatible with the experimental results.

Although the monohydride mechanism in Scheme 3 accommodates part of the experimental results, occurrence of the H–D exchange of the ruthenium hydride **2** with $(CH_3)_2CHOD$ is not compatible with the clean transfer of the hydrogen originating from the α-carbon of the donor alcohol to the imine carbon, which is expected if the hydride mechanism is operative. Thus, we propose a modified MPV mechanism involving the direct hydrogen transfer from an alkoxo ligand to a coordinated imine (Scheme 2) as a mechanism fully accommodating the experimental results.

Experimental

General Procedures. All the manipulations were performed under argon atmosphere by using Schlenk techniques. *cis*-[RuH_2-(PMe_3)$_4$] (**1**),[27] *cis*-[RuH(NH_3)(PMe_3)$_4$]PF_6 (**2**),[3a] *cis*-[Ru(NH_3)$_2$-(PMe_3)$_4$][PF_6]$_2$,[3a] *cis*-[RuClH(PMe_3)$_4$] (**6**),[28] *cis*-[RuH_2(PPh_3)$_4$] (**7**),[29] and *cis*-[RuClH(PPh_3)$_3$] (**8**)[30] were synthesized according to literature methods. $(CD_3)_2CHOH$ was prepared by hydrogenation of acetone-d_6 using Rh/C as a catalyst. $(C_2H_5)_2CDOH$ was prepared by treatment of diethyl ketone with $NaBD_4$. Solvents were dried, distilled, and stored under argon. All other reagents were used as received from commercial suppliers. ^1H (270.5 or 300.4 MHz, referenced to $SiMe_4$ via residual solvent protons) and $^{13}C\{^1H\}$ (67.9 or 75.4 MHz, referenced to $SiMe_4$ via solvent resonance) NMR were recorded on JEOL EX270 and JEOL AL300 spectrometers. $^{31}P\{^1H\}$ (109.4 MHz, referenced to 85% H_3PO_4 as an external standard) and ^2H (41.5 MHz, referenced to $Si(CD_3)_4$ via residual solvent deuterium) NMR were recorded on a JEOL EX-270 spectrometer. Gas chromatographic analyses were carried out on a Hitachi 263-30 instrument equipped with a TC-1701 (df = 0.25 μm, 0.25 mm i.d. × 30 m) or a Neutrabond-1 (df = 0.4 μm, 0.25 mm i.d. × 30 m) capillary column, using N_2 as a carrier gas.

Synthesis of [RuH(PMe_3)$_5$]PF_6 (5). Complex **1** (22.0 mg, 0.054 mmol) was dissolved in ether, and PMe_3 (0.010 mL, 0.096 mmol) and NH_4PF_6 (9.0 mg, 0.054 mmol) were added at −30 °C. After the reaction mixture was stirred for 1 h, the white precipitate was collected by filtration and washed with ether (5 mL × 3) and dried under vacuum. The spectroscopic features of this complex matched analogous compounds reported in the literature.[9,31] Yield: 29% (10.0 mg, 0.016 mmol). ^1H NMR (acetone-d_6): δ −11.3 (dquin, $^2J_{HP}$ = 74.2, 24.8 Hz, 1H, RuH), 1.3 (brs, PMe_3, 9H), 1.5–1.6 (brs, PMe_3, 36H). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −143 (sept, PF_6), −21.9 (quin, $^2J_{PP}$ = 26.4 Hz, PMe_3), −8.47 (d, $^2J_{PP}$ = 26.4 Hz, PMe_3).

General Procedures for Hydrogenation of Imines by Ru Complexes under Hydrogen Pressure. In a 100-mL stainless autoclave equipped with a magnetic stirrer and a glass tube connected to an argon line, Ru complex (0.02 mmol) was dissolved in 13 mL of solvent under argon atmosphere, and then the imine substrate (1.2 mmol) was added to the mixture. The autoclave was sealed and charged with hydrogen and placed in an oil bath at the set temperature. After the reaction mixture was stirred for an allotted time, the autoclave was cooled to room temperature and the pressure was then released. The reaction mixture was collected and analyzed by GC.

General Procedure for Transfer Hydrogenation of *N*-Benzylideneaniline with Secondary Alcohols by Ru Catalysts. In a 50-mL Schlenk tube, *N*-benzylideneaniline (0.362 g, 2.0 mmol) and K_2CO_3 (13.8 mg, 0.1 mmol) were added to the ruthenium catalyst (0.02 mmol) in secondary alcohol (15 mL) under argon atmosphere. After the mixture was stirred under reflux conditions for an allotted time, the product yield was determined by GC analysis of the solution phase. The identity of resulting amine was assessed by comparison with commercially available pure samples and by their fragmentation in GC/MS. The reactions in the absence of a base were performed in a similar manner except for treatment with K_2CO_3.

Transfer Hydrogenation of *N*-Benzylideneaniline with $(CH_3CH_2)_2CDOH$ by 2. In a 50-mL Schlenk tube, *N*-benzylideneaniline (72.5 mg, 0.4 mmol) and K_2CO_3 (13.8 mg, 0.1 mmol) were added to **2** (11.4 mg, 0.02 mmol) in $(CH_3CH_2)_2CDOH$ (98% D, 2.5 mL) under argon atmosphere. After the mixture was stirred under reflux conditions for 2 h, the yield was determined by GC without purification. The solvent was evaporated and a brown solid was obtained. The deuterium incorporation was analyzed by NMR spectroscopy.

Transfer Hydrogenation of *N*-Benzylideneaniline with $(CH_3)_2CHOD$ by 2. In a 50-mL Schlenk tube, *N*-benzylideneaniline (0.236 g, 1.3 mmol) and K_2CO_3 (9.0 mg, 6.5×10^{-2} mmol) were added to **2** (7.4 mg, 1.3×10^{-2} mmol) in $(CH_3)_2CHOD$ (98% D, 10 mL) under argon atmosphere. After the mixture was stirred under reflux conditions for 22 h, the yield was determined by GC without purification. The solvent was evaporated and a brownish solid was obtained. The deuterium incorporation was analyzed by NMR spectroscopy.

Transfer Hydrogenation of *N*-Benzylideneaniline with $(CD_3)_2CHOH$ by 2. In a 50-mL Schlenk tube, *N*-benzylideneaniline (0.181 g, 1.0 mmol) and K_2CO_3 (13.8 mg, 0.1 mmol) were added to **2** (11.4 mg, 2.0×10^{-2} mmol) in $(CD_3)_2CHOH$ (96% D, 8 mL) under argon atmosphere. After the mixture was stirred under reflux conditions for 18 h, the yield was determined by GC without purification. The solvent was evaporated and a brown solid was obtained. The deuterium incorporation was analyzed by NMR spectroscopy.

H–D Exchange between Complex 2 and $(CH_3)_2CHOD$. Complex **2** (17.1 mg, 3.0×10^{-2} mmol) was placed in an NMR sample tube equipped with a rubber septum cap and dissolved in THF-d_8 (0.3 mL) and $(CH_3)_2CHOD$ (0.3 mL) at room temperature. THF (2.4×10^{-3} mL, 3.0×10^{-2} mmol) was added as an internal standard. The tube was sealed and placed in an oil bath at 100 °C for 10 min and the NMR spectra were quickly taken. Deuterium content in the hydride region and yield of acetone were determined by peak integration of each signal in the ^{1}H NMR spectrum at room temperature.

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