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Transfer Hydrogenation of Aryl Ketones with Half-Sandwich Ru^{II} Complexes That Contain Chelating Diamines

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In a comparative study, half-sandwich complexes of Ru^{II} (**1**) with pyridine-based chelating diamine [N^N = 2-aminomethylpiperidine (ampi), **a**; 2-aminomethylpyridine (ampy), **b**; 8-aminoquaniline (aquan), **c**; 4,4′-dimethyl-2,2′-bipyridine (dbipy), **d**; 2,2′-bipyridine (bipy), **e**] or amine amide (Ts-ampi, **2a**) were synthesized by cleavage of [{(η^6-*p*-cymene)Ru(μ-Cl)Cl}$_2$] dimer and the resulting complexes were screened for their efficiency in the transfer hydrogenation (TH) of acetophenone in 2-propanol (IPA) at 82 °C or in water in HCOONa. Among the complexes, cationic **1a**, neutral **2a**, and **1b**, which bear ampi and ampy, were the most effective in terms of catalyst performance (turnover frequency values: 198, 6000, 23 h^{-1}, respectively).

Introduction

Since the pioneering work by Noyori and Ikariya et al.,[1] (η^6-arene)Ru^{II}-catalyzed asymmetric transfer hydrogenation (ATH) reactions have been the subject of increasing interest because of the advantages of this methodology over classical hydrogenation reactions.[2] Related reviews deal with the TH reaction mechanisms[3] and water-soluble organometallic complexes.[4] 2-Propanol (IPA), HCOOH/NEt_3, or HCOONa are the most frequently used hydrogen donors. Monotosylated diamines are among the most effective in terms of catalyst performance.[2] Rhodium and iridium complexes with various combinations of electron-rich ligands, such as vic-diamines,[5] tertiary phosphanes,[6] and N-heterocyclic carbenes (NHCs)[7] have enlarged the scope of TH reactions. Cleavage reactions of the [{(η^6-*p*-cymene)-Ru(μ-Cl)Cl}$_2$] dimer with bipyridyl-based ligands were reported to give water-soluble half-sandwich Ru^{II} complexes, which show good catalytic activity for TH of aryl ketones.[8] Baratta and co-workers and our group have independently reported a number of Ru^{II} complexes that bear the 2-aminomethylpyridine (ampy) group and have examined their excellent ability to catalyze the reduction of ketones.[9] In this report, we extend this approach to prepare water-soluble half-sandwich ruthenium complexes with pyridine-based bidentate N^N ligands and compare their efficiences in TH reactions. We decided to include 2-aminomethylpiperidine (ampi) because we anticipated that such functional groups (reduced pyridine and NH) would produce an N^N ligand with stronger σ donation than ampy. The ampi ligand is commercially available and relatively cheap, and its chiral version is known.[10]

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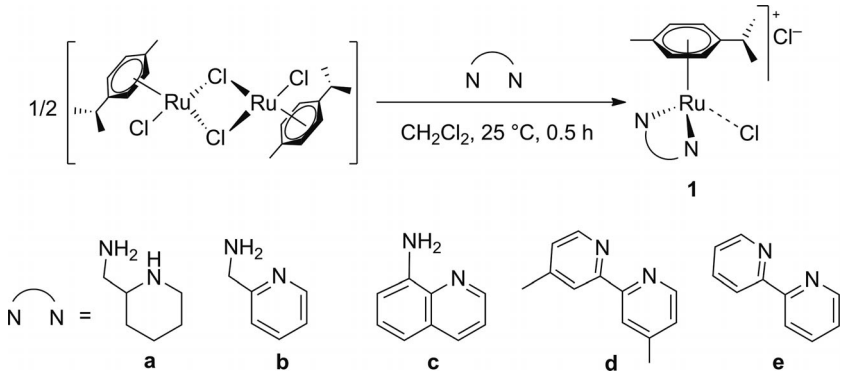
Results and Discussion

Cationic complexes (**1**) were prepared by the reaction of chelating ligands [N^N = 2-aminomethylpiperidine (ampi), **a**; 2-aminomethylpyridine (ampy), **b**; 8-aminoquinoline (aquan), **c**; 4,4′-dimethyl-2,2′-bipyridine (dbipy), **d**; 2,2′-bipyridine (bipy), **e**] with [{(η^6-*p*-cymene)Ru(μ-Cl)Cl}$_2$] as depicted in Scheme 1. The known complexes (**1b**, **1d**, **1e**) are also included for comparison purposes. The complexes can be stored in air for a long period of time and are soluble in DMSO, DMF, MeOH, and H_2O, and insoluble in apolar solvents such as hexane. The solubility (at 25 °C) of complexes in water is 120 (**1a**), 112 (**1b**), 93 (**1c**); 103 (**1d**), and 105 (**1e**) mg mL^{-1}. They were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The ^1H NMR spectrum clearly indicates the presence of *p*-cymene ligands in all complexes. In the case of complex **1a**, the *p*-cymene resonance appears in the usual range as two doublets at δ = 6.27 and 5.88 ppm. However, the *p*-cymene resonance of complex **1c** shows four different doublets for the aryl protons. All complexes gave ^{13}C NMR spectra that correspond to the proposed formulation.

Description of Structure

An ORTEP representation of complex **1a** is shown in Figure 1. The complex crystallizes in an orthorhombic noncentrosymmetric system with Z = 4 in space group $P2_12_12_1$. The significant bond lengths and bond angles are listed in Table 1. The cationic mononuclear complex con-



Scheme 1. Synthesis of the cationic ruthenium–arene complexes.

sists of a ruthenium atom coordinated to the η^6-*p*-cymene ligand that occupies the facial coordination site, to the two nitrogen atoms of the 2-aminomethylpiperidine ligand, and to a chlorine atom, with the coordination geometry of ruthenium being a pseudotetrahedral arrangement (Figure 1). In the crystal structure, one chlorine atom exists as a counterion. The ruthenium atom is situated 1.670 Å away from the centroid of the *p*-cymene moiety. The interaction distance is similar to those found in cationic Ru complexes, $[(C_6Me_6)Ru(phen)(Cl)]^+$ and $[(C_6Me_6)Ru(phen)(OH_2)]^{+2}$.[8d]

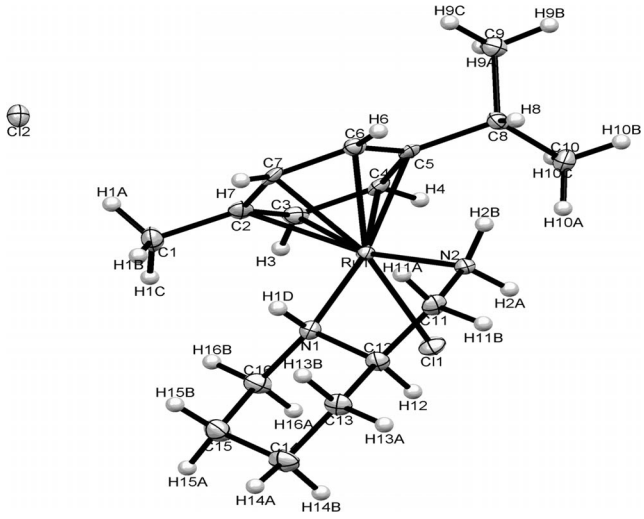


Figure 1. A view of complex **1a** showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Table 1. Selected bond lengths and angles [°] of complex **1a**.

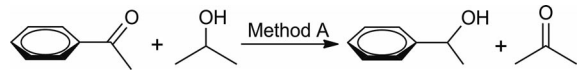
Bond lengths [Å]		Bond angles [°]	
Ru1–N2	2.126(3)	N2–Ru1–N1	79.47(11)
Ru1–N1	2.153(3)	N2–Ru1–C6	90.69(12)
Ru1–C6	2.165(3)	N1–Ru1–C6	119.89(12)
Ru1–C7	2.169(3)	N2–Ru1–C7	114.71(12)
Ru1–C4	2.188(3)	N1–Ru1–C7	94.43(12)
Ru1–C3	2.195(3)	N2–Ru1–C4	122.51(12)
Ru1–C5	2.205(3)	N1–Ru1–C4	157.63(12)
Ru1–C2	2.225(4)	N2–Ru1–C3	160.42(12)
Ru1–Cl1	2.4059(8)	N1–Ru1–C3	120.09(12)
C12–N1	1.491(4)	N2–Ru1–C5	93.95(12)

Ru–C distances in η^6-arene fall within the usual range 2.165(3)–2.406(9) Å and are quite similar to other related Ru–η^6-arene complexes.[11] The two Ru–N bond lengths are slightly different [2.125(2) and 2.155(3) Å]. The Ru–Cl bond length of 2.4059(8) Å is also essentially similar and quite comparable to those of other cationic ruthenium complexes.[12] The bite angle of the 2-aminomethylpiperidine ligand is 79.47(11)°.

Catalytic Studies

All complexes **1**–**2a** were studied for the transfer hydrogenation of acetophenone to give phenylethanol in 2-propanol at 82 °C (Table 2). Over a 30 min period the catalytic activity decreases in the order **1a** > **1b** > **1c** > **1d** ≈ **1e**. The highest activity was observed for the 2-aminomethylpiperidine derivative **1a**. For example, comparison of ampi (**1a**) and the ampy (**1b**) complexes clearly indicated their differences (Table 2, entries 1–4).[9g] On the other hand, aquan analogue **1c** was less active under the same conditions. Apparently, electronic effects and the presence of N^N ligand increased the activity of the cationic complex. Despite the different electronic effects of the 4-CH_3 and 4-H substituents of the bipy skeleton on **1d** and **1e**, respectively, the activity of **1d** and **1e** was surprisingly very similar. Consistent

Table 2. Catalytic activity for transfer hydrogenation of acetophenone catalyzed by Ru^{II} complexes.[a]



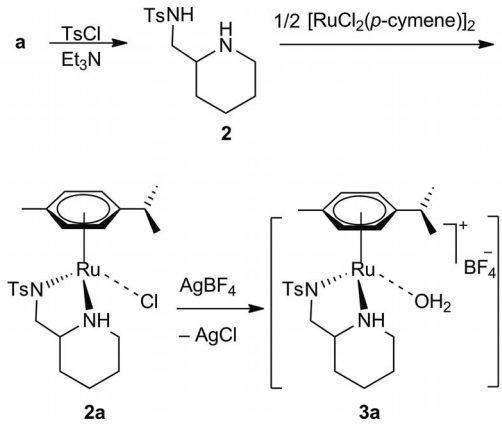
Entry	Cat.	*t* [min]	Conversion [%][b]	TOF[c]
1	**1a**	30	99	198
2	**1a**	15	66	–
3	**1b**	30	52	23
4	**1b**	15	03	–
5	**1c**	30	46	17
6	**1d**	30	34	11
7	**1e**	30	31	9
8	$[\{p\text{-cymRuCl}_2\}_2]$	30	05	0.4

[a] Method A: [S]/[cat] = 100, 82 °C, KOH, in IPA. [b] Based on 5 min conversion. [c] Turnover frequency (TOF) in mol mol^{-1} h^{-1}.

with the previous observations, ligands that bore N(H) and NH_2 entities (**1a**–**1c**) showed higher activities than the complexes without (**1d**, **1e**). Under the same conditions, the dimer [{(η^6-*p*-cymene)Ru(μ-Cl)Cl}$_2$] performed poorly with 5% conversion (entry 8).

Since the arene–ruthenium complexes synthesized here are water-soluble, we also assessed their TH activity in the presence of formic acid and sodium formate as a hydrogen-donor source in water. We surveyed the effect of bases, the catalyst loading, and reaction times on the TH of acetophenone by using complex **1a** as a ruthenium source (Table 3). Ogo and co-workers reported the TH of ketones by HCOONa or HCOOH in water with water-soluble half-sandwich Ru^{II} complexes. The best results were obtained at pH = 3.8 (i.e., the pK_a of formic acid) for an equimolar radio of HCOOH/HCOONa (2.5 equiv. of each relative to the substrate).[8c] Under these conditions, the product was obtained in 92% conversion within 4 h (Table 3, entry 1). The use of 2.5 equiv. of HCOONa or HCOOH led to lower conversions (72 and 10%, respectively). A decrease in HCOONa to 1.0 equiv. led to a decrease in conversion (entry 7). When the catalyst loading decreased from 1 to 0.01%, a slightly lower conversion was obtained (entries 1 and 8). To test the catalyst performance at lower temperatures, the transfer hydrogenation of acetophenone was determined at temperatures from 25–82 °C. Temperature-dependent studies between 25, 50, and 65 °C afforded moderate yields (entries 9–11).

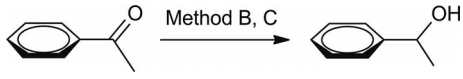
We also performed an additional experiment to assess the relative reactivity of complex **2a** toward transfer hydrogenation of acetophenone. The reaction of [{(η^6-*p*-cymene)-Ru(μ-Cl)Cl}$_2$] with the monotosylated *N*-tosyl-1-piperidin-2-ylmethanamine at 65 °C in chloroform gave a brown precipitate, which was purified by column chromatography on silica gel by using dichloromethane as eluent. Ligand **2** and orange complex **2a** were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.



Having isolated complex **2a**, we then carried out catalytic studies in TH and compared the methods used above. As can be seen from the data shown in Table 3, **2a** is very active in transfer hyrogenation in water (Table 3, entry 12) when catalyst loadings of 10^{-1} or even 10^{-2} mol-% were used (entries 13 and 14); however, the activity dramatically decreased at lower catalyst loadings. Aqua complex **3a**, generated in situ with $AgBF_4$ in aqueous solution, was tested in TH by using acetophenone as a substrate. The effect of the aqua ligand on the activity with **3a** was not noticeable (entry 15). Previously, the beneficial effect of donor substituents at the arene ligand was studied by Süss-Fink et al. and Renaud et al.[5,8f] They observed that *p*-cymene gave the best result on TH and it was proposed that *p*-cymene ligand is the best compromise between steric effects and electron density on the ruthenium. We also performed the catalytic study in the presence of free *p*-cymene in methods B and C, but the conversion did not differ significantly. This indicates that *p*-cymene does not dissociate during the catalytic events that involve **1a** or **2a**.

To further explore the effectiveness of catalyst **1a** and **2a** on other substrates, 4-chloroacetophenone, 2-chloroacetophenone, 4-bromoacetophenone, 4-floroacetophenone, 4-methoxyacetophenone, benzophenone, 2-acetylbiphenyl, cyclohexanone, and 3,4-dimethylacetophenone were also investigated under identical conditions; the results are summarized in Table 4. Ru^{II} complexes were generally more efficient catalysts when electron-withdrawing substituents such as Cl or Br were present at the *para* or *ortho* position of the aryl ring of the ketone. When an electron-donating substituent such as OCH_3 or CH_3 was introduced into the aryl ring of the ketone, the catalytic activity decreased. In the cases of aliphatic ketones, the rate of reaction decreased even more (entries 10–13).

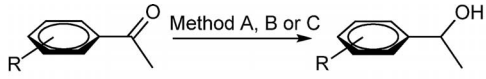
Table 3. Screening of bases and/or hydrogen donor in water.

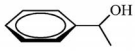
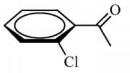
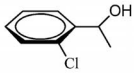
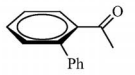
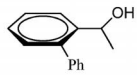
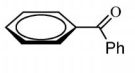
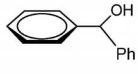
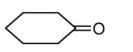
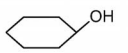
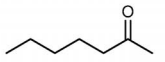
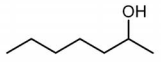
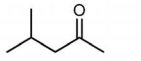
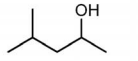
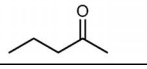
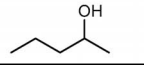


Entry	Cat. [mol-%]	Hydrogen donor [mmol]	*t* [min]	Conv. [%]
1	1	NaO_2CH/HCO_2H (2.5:2.5)	240	92[a]
2	1	NaO_2CH/HCO_2H (2.5:2.5)	960	99[a]
3	1	NaO_2CH(2.5)	240	77[a]
4	1	NaO_2CH(2.5)	960	93[a]
5	1	HCO_2H (2.5)	240	10[a]
6	1	HCO_2H (2.5)	960	35[a]
7	1	NaO_2CH(1.0)	240	46[a]
8	0.01	NaO_2CH/HCO_2H (2.5:2.5)	240	36[a]
9	1	NaO_2CH/HCO_2H (2.5:2.5)	240	02[b]
10	1	NaO_2CH/HCO_2H (2.5:2.5)	240	56[c]
11	1	NaO_2CH/HCO_2H (2.5:2.5)	240	86[d]
12	1	NaO_2CH/HCO_2H (2.5:2.5)	1	100[e]
13	0.1	NaO_2CH/HCO_2H (2.5:2.5)	1	74[e]
14	0.01	NaO_2CH/HCO_2H (2.5:2.5)	1	43[e]
15	1	NaO_2CH/HCO_2H (2.5:2.5)	1	98[e,f]
16	1	NaO_2CH/HCO_2H (2.5:2.5)	240	90[a,g]
16	1	NaO_2CH/HCO_2H (2.5:2.5)	1	94[e,g]

[a] Method B: **1a**, 82 °C, H_2O. [b] Reaction temperature: 25 °C. [c] At 50 °C. [d] At 65 °C. [e] Method C: **2a**, 82 °C, H_2O. [f] Complex **3a** was used instead of **2a**. [g] Free *p*-cymene (2.5 mmol) was added to the aqueous solution.

Table 4. Comparison of the methods for conversion of different substrates.



Entry	Substrate	Product	Method A[a,b]	Method B[a,b]	Method C[c]
1			99	92	100
2			94	92	95
3			99	98	99
4			85	90	91
5			97	94	93
6			62	87	88
7			65	82	86
8			66	76	71
9			67	69	72
10			73	78	83
11			61	65	67
12			59	51	68
13			54	49	60

[a] Conversion in %. [b] Method A: [S]/[cat] = 100, **1a**, 82 °C, KOH, IPA, 0.5 h; Method B: [S]/[cat] = 100, **1a**, 82 °C, HCO_2H/HCO_2Na (2.5 mmol/2.5 mmol), H_2O, 4 h; Method C: [S]/[cat] = 100, **2a**, 82 °C, HCO_2H/HCO_2Na (2.5 mmol/2.5 mmol), H_2O, 1 min.

Catalyst Recycling

We examined the possibility of reusing catalysts **1a** and **2a** for the transfer hydrogenation of acetophenone, and the reactions were conducted using method B and method C. After the first reaction, ethyl ether was added to extract the organic compounds, and the catalyst immobilized in the water phase was reused directly. Fresh substrates and sufficient distilled water were added to the water phase that contained **1a** or **2a** to bring the volume to 4.0 mL. The yields for the second, third, and fourth cycles were 84, 68, and 61%, respectively (Table 5). Catalyst **1a** appears to be reusable for four cycles of the transfer hydrogenation of acetophenone; however, on the fifth cycle, the conversion dropped to 35%. But after the fifth cycle, the addition of 5 equiv. formic acid and sodium formiate to the water phase increased the conversion to 80% within 4 h. This result demonstrated that complex **1a** remains active after the fifth run.

Table 5. Reusabilty of catalyst **1a** for the transfer hydrogenation of acetophenone using methods B and C.[a]

Cycles	1st[b]	2nd[b]	3rd[b]	4th[b]	5th[b]	6th[b]
Method B	92	84	68	61	35	20 (80)[c]
Method C	100	54	13 (15)[c] (14)[d]	–	–	–

[a] Method B: [S]/[cat] = 100, **1a**, 82 °C, HCO_2H/HCO_2Na (2.5 mmol/2.5 mmol), H_2O, 4 h; Method C: [S]/[cat] = 100, **2a**, 82 °C, HCO_2H/HCO_2Na (2.5 mmol/2.5 mmol), H_2O, 1 min. [b] % Conversion. [c] HCO_2H/HCO_2Na (2.5 equiv/2.5 equiv.) was added to the water phase. [d] Free *p*-cymene (2.5 mmol) was added to the aqueous solution.

In the series of experiments that followed method C, the reason for this decrease is different. During the second run, the color of solution turned yellow to green, a phenomenon that provided evidence of the decomposition of catalyst **2a**, because the addition of hydrogen donor does not afford any conversion. In addition, the rate of conversion did not change in the presence of free *p*-cymene (Table 5).

Conclusion

We have found that ampi is a well-suited bidentate ligand both in cationic and neutral Ru^{II} complexes for catalyzing transfer hydrogenation. The electron-donating ring and the presence of NH and NH_2 groups increases the yield and solubility in water. It is assumed that this ligand offers extra hydrogen bonds near the metal center. The synthesis of rhodium and iridium complexes with the ampi ligand and chiral versions of ampi and Ts-ampi are in progress in our laboratories.

Experimental Section

General: Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture. All solvents and chemicals were used as received. Starting compounds and reagents were obtained from Merck, Fluka, Alfa Aesar, and Acros Organics; 2-aminomethylpiperidine was obtained from Alfa Aesar; and solvents such as dichloromethane, ethanol, diethyl ether, toluene, *N*,*N*-dimethylformamide, hexane, and pentane were obtained from Merck and Ridel de Haen. Compounds **1e** and **1d** and $[\{(p\text{-cymene})RuCl_2\}_2]$ were prepared according to the literature.[13,14] Melting points were recorded with a Gallenkamp electrothermal melting-point apparatus. Elemental analysis data were recorded with CHNS elemental analysis. ^1H and ^{13}C NMR spectra were recorded with a Varian AS 400 Mercury instrument. $CDCl_3$ and $[D_6]$DMSO were employed as solvents.

$[(\eta^6\text{-}C_{10}H_{14})Ru(ampi)Cl]Cl$ (1a): 2-Aminomethylpiperidine (**a**; 0.228 g, 2.0 mmol) was added to a suspension of $[\{(\eta^6\text{-}C_{10}H_{14})\text{-}RuCl_2\}_2]$ (0.612 g, 1.0 mmol) in dichloromethane (10 mL), and the resulting solution was stirred for 4 h at room temperature. The yellow solution thus obtained was filtered to remove any solid impuri-

ties, and the filtrate was concentrated to half of its volume. The concentrated solution was saturated with diethyl ether and left in the refrigerator for crystallization. Slowly, a microcrystalline product separated, which was removed by filtration, washed with diethyl ether, and dried under vacuum. Yield 0.75 g, 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.27 [d, J = 6 Hz, 1 H, $C_{10}H_{14}(C_6H_4)$], 5.88 [d, J = 6 Hz, 1 H, $C_{10}H_{14}(C_6H_4)$], 5.63 [d, J = 6 Hz, 1 H, $C_{10}H_{14}(C_6H_4)$], 5.54 [d, J = 5.6 Hz, 1 H, $C_{10}H_{14}(C_6H_4)$], 3.39 (d, J = 0.8 Hz, 2 H, NCH_2), 3.19 (m, 1 H, piperidin-*H*), 3.07 {m, 1 H, $C_{10}H_{14}[CH(CH_3)_2]$}, 2.87 (m,1 H, piperidin-*H*), 2.72 (m, 1 H, piperidin-*H*), 2.63 (m, 1 H, piperidin-*H*), 2.50 [s, 3 H, $C_{10}H_{14}(CH_3)$], 2.21 (m, 1 H, piperidin-*H*), 1.95 (m, 1 H, piperidin-*H*), 1.86 (m, 1 H, piperidin-*H*), 1.60 (m, 2 H, piperidin-*H*), 1.31 {d, J = 3.6 Hz, 6 H, $C_{10}H_{14}[CH(CH_3)_2]$} ppm. ^{13}C NMR (100 MHz,$CDCl_3$): δ = 103.4, 100.2, 85.9, 83.6, 79.9, 79.0 [$C_{10}H_{14}(C_6H_4)$], 60.8 (NCH_2), 53.2, 50.5, 30.9, 26.5, 26.2, 23.8, 22.3, 18.7 {piperidin-*C*, $C_{10}H_{14}[CH(CH_3)_2]$, $C_{10}H_{14}(CH_3)$} ppm. $C_{16}H_{27}Cl_3N_2Ru$ (454.83): calcd. C 42.25, H 5.92, N 6.16; found C 42.33, H 5.94, N 6.11.

[(η^6-$C_{10}H_{14}$)Ru(aquan)Cl]Cl (1c): Compound **1c** was prepared by following the procedure for **1a** by using [{(η^6-$C_{10}H_{14}$)$RuCl_2$}$_2$] (0.612 g, 1.0 mmol) and 8-aminoquaniline (0.288 g, 2.0 mmol). Yield 0.87 g, 89%. ^{1}H NMR (400 MHz, D_2O): δ = 9.48 (d, J = 5.2 Hz, 1 H, quaniline-*H*) 8.42 (d, J = 8.4 Hz, 1 H, quaniline-*H*), 7.80 (d, J = 8.4 Hz, 1 H, quaniline-*H*), 7.75 (d, J = 7.2 Hz, 1 H, quaniline-*H*), 7.65 (dd, J = 3. 6 Hz, 1 H, quaniline-*H*), 7.57 (t, J = 7.4 Hz, 1 H, quaniline-*H*), 5.96 [d, J = 6 Hz, 1 H, $C_{10}H_{14}(C_6H_4)$], 5.85 [d, J = 6 Hz, 1 H, $C_{10}H_{14}(C_6H_4)$], 5.73 [d, J = 5.6 Hz, 1 H, $C_{10}H_{14}(C_6H_4)$], 5.65 [d, J = 5.6 Hz, 1 H, $C_{10}H_{14}(C_6H_4)$], 2.55 {m, 1 H, $C_{10}H_{14}[CH(CH_3)_2]$}, 2.03 [s, 3 H, $C_{10}H_{14}(CH_3)$], 0.98, 0.83 {d, J = 3.6 Hz, 3 H, $C_{10}H_{14}[CH(CH_3)_2]$} ppm. ^{13}C NMR (100 MHz, D_2O): δ = 156.3, 145.5, 139.6, 138.1, 129.5, 128.7, 128.5, 127.6, 124.3 (quaniline-*C*), 110.4, 101.1, 85.1, 83.6, 82.9, 82.3 [$C_{10}H_{14}(C_6H_4)$], 30.6, 21.5, 21.3, 18.0 {$C_{10}H_{14}[CH(CH_3)_2]$, $C_{10}H_{14}(CH_3)$} ppm. $C_{16}H_{22}Cl_3N_2Ru$ (454.83): calcd. C 46.97, H 4.56, N 5.77; found C 46.89, H 4.54, N 5.81.

Ts-ampi (2): A solution of 2-aminomethylpiperidine (**a**; 2.28 g, 20.0 mmol) and triethylamine (5.7 mL, 40.0 mmol) in dry THF (20 mL) was cooled to –5 °C. *p*-Tolylsulfonyl chloride (20.0 mmol) was successively added dropwise to the cold solution while maintaining the reaction temperature below 0 °C. The resulting mixture was stirred at room temperature for 12 h. The organic layer was separated and washed with 1 M aqueous H_3PO_4 (1.0 mL) followed by saturated aqueous $NaHCO_3$ (2.5 mL), dried with anhydrous Na_2SO_4, filtered, and concentrated to obtain product **2**, which is a known compound and was fully determined according to the previously reported data.[10] Yield 5.1 g, 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 [d, J = 8 Hz, 2 H, *p*-$(CH_3)C_6H_4SO_2$], 7.27 [d, J = 8 Hz, 2 H, *p*-$(CH_3)C_6H_4SO_2$], 3.65 (d, J = 12.4 Hz, 1 H, NCH_2), 3.40–3.35 (m, 2 H, piperidin-*H*), 3.02 (d, J = 12.4 Hz, 1 H, NCH_2), 2.91 (m, 1 H, piperidin-*H*), 2.39 [m, 3 H, *p*-$(CH_3)C_6H_4SO_2$], 1.98–1.75 (m, 5 H, piperidin-*H*), 1.47 (m, 1 H, piperidin-*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.6, 135.2, 129.9, 127.6, [*p*-$(CH_3)C_6H_4SO_2$], 55.6, 45.2, 28.2, 27.4, 23.8, 22.2, 21.7 [piperidin-*C*, *p*-$(CH_3)C_6H_4SO_2$] ppm. $C_{13}H_{20}N_2O_2S$ (268.37): calcd. C 58.18, H 7.51, N 10.44; found C 58.23, H 7.49, N 10.41.

Synthesis of [(η^6-$C_{10}H_{14}$)Ru(Ts-ampi)Cl] (2a): Compound **2a** was prepared by following the procedure for **1a** by using [{(η^6-$C_{10}H_{14}$)-$RuCl_2$}$_2$] (0.612 g, 1.0 mmol) and *N*-tosyl-2-aminomethylpiperidine (0.536 g, 2.0 mmol). Yield 0.78 g, 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 [d, J = 2 Hz, 2 H, *p*-$(CH_3)C_6H_4SO_2$], 7.06 [d, J = 2 Hz, 2 H, *p*-$(CH_3)C_6H_4SO_2$], 5.75 [s, 1 H, $C_{10}H_{14}(C_6H_4)$], 5.46 [s, 1 H, $C_{10}H_{14}(C_6H_4)$], 5.24 [d, J = 0.9 Hz, 2 H, $C_{10}H_{14}(C_6H_4)$], 3.67 (d, J = 3.1 Hz, 1 H, NCH_2), 3.12 (m, 1 H, piperidin-*H*), 2.97 {m, 2 H, piperidin-*H*, $C_{10}H_{14}[CH(CH_3)_2]$}, 2.85 (m, 1 H, piperidin-*H*), 2.37 (m, 1 H, piperidin-*H*), 2.61 [s, 3 H, *p*-$(CH_3)C_6H_4SO_2$], 2.22 (m, 1 H, piperidin-*H*), 2.14 [s, 3 H, $C_{10}H_{14}(CH_3)$], 1.76–163 (m, 2 H, piperidin-*H*), 1.40 (m, 1 H, piperidin-*H*), 1.27 {d, J = 1.8 Hz, 6 H, $C_{10}H_{14}[CH(CH_3)_2]$}, 1.20 {d, J = 3.6 Hz, 6 H, $C_{10}H_{14}[CH(CH_3)_2]$} ppm. ^{13}C NMR (100 MHz,$CDCl_3$): δ = 139.3, 139.2, 127.5, 126.6 [*p*-$(CH_3)C_6H_4SO_2$], 103.7, 98.2, 83.6, 81.8, 79.1, 79.0 [$C_{10}H_{14}(C_6H_4)$], 65.4 (NCH_2), 54.2, 53.6, 29.7, 27.6, 27.1, 23.8, 22.0, 20.9, 20.3, 18.7 {piperidin-*C*, *p*-$(CH_3)C_6H_4SO_2$, $C_{10}H_{14}$-$[CH(CH_3)_2]$, $C_{10}H_{14}(CH_3)$} ppm. $C_{23}H_{34}Cl_2N_2O_2RuS$ (574.56): calcd. C 48.08, H 5.96, N 4.88; found C 48.03, H 5.97, N 4.91.

X-ray Structural Analyses of the Complex: Diffraction data for the complex were collected with a Bruker SMART APEX CCD diffractometer equipped with a rotation anode at 296(2) K by using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SAINT[15] program package. For further crystal and data collection details, see Table 1. Structure solution was found with the SHELXS-97[16] package by using direct methods refined with SHELXL-97[17] against F^2, first using isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure model on calculated positions. Geometric calculations were performed with Platon.[18]

Hydrogen-Transfer Catalytic Experiments. Method A: Tested complex **1** (0.01 mmol) was dissolved in a solution of KOH (1.0 mmol), substrate (1.0 mmol), and 2-propanol (4.0 mL) in a Schlenk tube under air. The solution was heated to 82 °C for 0.5 h. The percentage conversion was monitored by ^{1}H NMR spectroscopy and as an average of two trials.

Method B: Complex **1a** (0.01 mmol) was dissolved in a solution of NaO_2CH (2.5 mmol), HCO_2H (2.5 mmol), and water (4.0 mL) in a Schlenk tube under air. Subsequently, substrate (1.0 mmol) was added with an Eppendorf pipette. The solution was heated to 82 °C for 4 h. Percentage conversion was monitored by ^{1}H NMR spectroscopy and as an average of two trials.

Method C: Complex **2a** (0.01 mmol) was dissolved in a solution of NaO_2CH (2.5 mmol), HCO_2H (2.5 mmol), and water (4.0 mL) in a Schlenk tube under air. Subsequently, substrate (1.0 mmol) was added with an Eppendorf pipette. The solution was heated to 82 °C for 1 min. Percentage conversion was monitored by ^{1}H NMR spectroscopy and as an average of two trials.

Recycling Studies with 1a and 2a: The flask was charged with catalyst, acetophenone (1.0 mmol), NaO_2CH (2.5 mmol), HCO_2H (2.5 mmol), and water (4.0 mL). The solution was heated to 82 °C. After cooling to room temperature, the organic products were extracted by using diethyl ether. The aqueous phase was then transferred to a new reaction flask for the ext cycle. Yields were determined by ^{1}H NMR spectroscopy for an average of two runs.

CCDC-76046 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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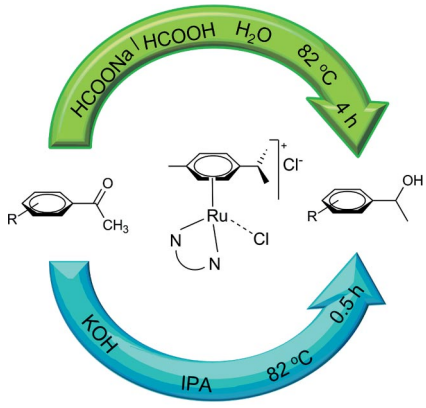
Arene–Ruthenium(II) Complexes

A series of N^N complexes of ruthenium(II) have been isolated and structurally characterized. These complexes were found to be amenable catalysts for the transfer hydrogenation of ketones.



Keywords: Hydrogenation / Ruthenium / N ligands / Ketones / Arenes

