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Novel *N*-coordinate half-sandwich ruthenium(II) arene complexes bearing sulfonamide fragments: Catalytic activities in the TH of acetophenone derivatives

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ABSTRACT

The novel cationic *N*-coordinate ruthenium(II)/arene complexes (**6**–**10**) were prepared from the starting complex [$RuCl_2$(*p-cymene*)]$_2$ dimer. The structures of the [(*p*-cymene)RuLCl]Cl (L = *N*-arenesulfonyl-4,5-dimethyl-*o*-phenylenediamines) complexes were elucidated by FT-IR, ^{1}H-NMR, ^{13}C-NMR, ionic conductivity techniques, and elemental analysis methods. The **6**–**10** complexes were applied as catalyst in the transfer hydrogenation (TH) of ketones. The catalytic tests showed that all the complexes are moderate catalysis precursors. Especially, {[*N*-benzenesulfonyl-4,5-dimethyl-*o*-phenylenediamine]-(*p*-cymene)-di-chloro-ruthenium(II)} (**8**) and {[*N*-4-chlorobenzenesulfonyl-4,5-dimethyl-*o*-phenylenediamine]-(*p*-cymene)-di-chloro-ruthenium(II)} (**9**) compounds were found to be a good catalysts in comparison to the others giving the corresponding alcohols in a good turnover frequency value of **1534** and **1731** h^{-1}, respectively.

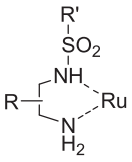
1. Introduction

The ligands bearing sulfonamide moiety are widely used as a precursor complex in coordination chemistry [1,2]. In addition, the complexes of bioactive sulfonamide-based ligands have also been reported [3]. Moreover, the Pd(II) complexes of NHC–*N* donor hybrid ligands bearing the sulfonamide group were reported [4]. Furthermore, the properties of ligands and complexes containing sulfonamide have been investigated in the field of luminescence, molecular modelling, and in antimicrobial and analytical applications [5–8]. In addition to the different complexes bearing sulfonamides having various catalytic effects, they can also be used as homogeneous or heterogeneous catalysts in various organic reactions, for example, in the oxidation of benzyl alcohol, olefin metathesis, chiral and achiral transfer hydrogenation, Henry reaction etc. [9–16].

In recent times, the ruthenium(II) or rhodium(III) complexes of C_2-symmetric bis(sulfonamide)-cyclohexane-1,2-diamine-RhCp* and chiral substituted aromatic monosulfonamide were synthesized and used as catalysts for ATH in isopropanol or water [17,18]. Moreover, the syntheses of optically active β-hydroxysulfonamides have been reported with asymmetric TH of the corresponding β-ketosulfonamides using the Ru–TsDPEN–HCOOH–Et_3N catalytic system [19]. In addition, when the Ru(II) complexes of TsDPEN were used in TH, catalytic activity was found to increasingly depend on the importance of the N–H bond [20].

Herein, a series of cationic *N*-coordinate Ru(II) arene complexes bearing sulfonamide moiety were prepared with an easy and general method. All the compounds (**1**–**10**) were characterized by using NMR, FT-IR, elemental analysis and ionic conductivity techniques. A cationic Ru(II) arene complexes of 4,5-dimethyl-*o*-phenylenediamine derivatives bearing sulfonamide fragment is used as catalyst in the TH of ketones for the first time.

The sulfonamide group can be easily used in the deprotonation of amide NH [21] or vice versa [22]. All the measurements indicated that the proposed structure of all the complexes was observed as a



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type bond. The synthesized Ru(II) complexes were tested as catalysts in the TH of acetophenones.

2. Results and discussion

2.1. Syntheses of all compounds

The synthesis and reaction routes to the ligands and to their corresponding Ru(II) complexes are presented in Figs. 1 and 2. Ligands **1**–**5** were formed by the reaction of 4,5-dimethyl-*o*-phenylenediamine with arylsulfonyl chlorides in the presence of triethylamine in THF (Fig. 1). New cationic ruthenium complexes **6**–**10** were also obtained by the reaction of **1**–**5** with $[RuCl_2(p\text{-cymene})]_2$ in methyl alcohol (Fig. 2). All ligands and their complexes were characterized by ^{1}H-NMR, ^{13}C-NMR, FT-IR, elemental analysis and molar conductance methods.

2.2. NMR spectra

In the ^{1}H-NMR spectra for **1**–**5**, the -H_a, -H_b protons were observed as doublets in a 2:2 ratio at around δ 6.91–7.78 ppm. The -H_1 and -H_2 protons were observed as singlets in a 1:1 ratio at around δ 6.15–6.56 ppm. The -H_p and -H_t protons belonging to the methyls were observed as singlets in a 1:1 ratio at around δ 1.90–2.12 ppm. In (**c**) position, the peaks belonging to the -*p*-CH_3, *o*-CH_3, -*p*-OCH_3 and $-C(CH_3)_3$ protons and carbons are shown in Figures S1-5.

N-coordinated complexes were used as nucleophiles to cleave the $[RuCl_2(p\text{-cymene})]_2$ dimer and the resultant *N*-coordinated ruthenium complexes (**6**–**10**) occurred in high yields. All the complexes (**6**–**10**) were isolated as dark green or black as stable in the solid state. In the ^{1}H-NMR spectra for **6**–**10,** the protons relating to *p*-cymene group were observed at around 1.18–1.28 ppm as doublet, 2.08–2.18 ppm as singlet, 2.91–2.92 ppm as multiplet, 5.34–5.77 ppm as doublet, 5.47–5.81 ppm as doublet, respectively. In the ^{13}C-NMR spectra for the Ru(II) complexes (**6**–**10**), the peaks in (**c**) position belonging to the -*p*-CH_3, *o*-CH_3, -*p*-OCH_3 and $-C(CH_3)_3$ protons and carbons were obtained at 25.6, 26.7, 55.7, 31.1, 31.0 ppm, respectively. The peaks showed a general shift towards lower fields as compared to their respective ligands. The NMR spectra of all compounds are attached in Figures S1-5 as supplementary materials.

2.3. Infrared spectra

In the IR spectra for **1**–**10**, the *N*–*H* stretching frequency peaks belonging to the sulfonamide groups appeared at 3339, 3334, 3335, 3383, 3342 cm^{-1} for **1**–**5**, at 3151, 3200, 3212, 3218, 3205 cm^{-1} for **6**–**10** and NH_2 stretching frequency peaks were observed at 3419, 3417, 3414, 3470, 3425 cm^{-1} for **1**–**5**, at 3243, 3253, 3280, 3296, 3278 cm^{-1} for **6**–**10** in the spectra.

2.4. Ionic conductivity

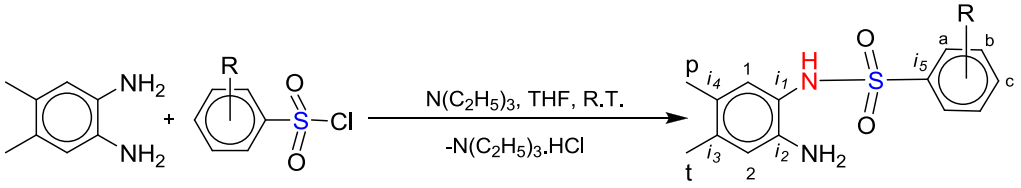
Conductance measurements were made at ambient temperature on 1.00×10^{-3} M samples in methyl alcohol. A solution of KCl (1.00×10^{-3} M) was used as the standard. The results of molar conductance were determined as 92.5 μS for KCl, 84.8 μS for **6**, 85.1 μS for **7**, 87.9 μS for **8**, 88.2 μS for **9**, and 85.4 μS for **10**. The results are consistent with the proposed structure of complexes. At the same time, $[Ru(R^I\text{-}NHSO_2\text{-}R)]$ type compounds are also available in the literature [23].

2.5. Catalysis studies

In recent times, the TH of ketones to alcohols has been extensively investigated [16,23–30]. At the same time, studies are continuously being aimed at obtaining better catalysts. In the present work, we successfully synthesized a series of novel ruthenium(II) arene complexes bearing sulfonamide fragments (**6**–**10**). The complexes were used as catalysts for the TH of acetophenone derivatives. The reaction conditions for this important process are economic, relatively mild and environmentally friendly. The volatile acetone product can also be easily removed to shift an unfavourable equilibrium. As the starting point, the performances of the catalysts in the TH were screened by using acetophenone as a model substrate.

In the TH reaction, the base facilitates the formation of ruthenium alkoxide by abstracting proton from the alcohol and subsequently alkoxide undergoes β-elimination to give ruthenium hydride, which is an active species in this reaction. Since the base facilitates the formation of ruthenium alkoxide by abstracting the proton from isopropanol, different bases were used as promoters in the TH of ketones. Acetophenone was kept as a test substrate and allowed it to react in isopropanol with catalytic quantities of complexes **9** (model complex) in the presence of different bases like KOH, NaOH, KO^tBu and K_2CO_3. NaOH and KOH are known to yield better conversions than K_2CO_3 and KO^tBu in TH reactions [16,23]. The stronger the base, the higher the general conversion rankings: KOH > NaOH > KO^tBu > K_2CO_3 (Table 1). In the absence of base, no TH was observed. Therefore, KOH was selected as the base in all subsequent studies. Additionally, in the absence of catalyst, the conversion of TH for acetophenone was founded 16% for 120 min with excess KOH. In addition, the $[RuCl_2(p\text{-cymene})]_2$ complex were tested as catalyst and the conversion were observed as 45% under this reaction condition.

With these optimized condition, the catalytic experiments results are shown in Tables 2 and 3. The conversion of 4-chloroacetophenone is the fastest, giving complete conversion to the corresponding alcohol at 120 min under the selected operating conditions (Table 2). It was observed that the activation period was short for catalyst **9** with an S/C = 500/1 ratio; a 46% conversion rate was achieved in only 10 min with 4-chloroacetophenone (TOF = **1390** h^{-1}). Under the same reaction conditions, catalyst **6**, **7**, **8**, **10** had TOF values of **1340**, **1210**, **1307**, **1222** h^{-1} at 10 min with



R= 4-OMe (**1**); 2,4,6-trimethyl (**2**); 4-H (**3**); 4-Cl (**4**); 4-*tert*-butyl (**5**)

Fig. 1. Synthesis of the *N*-arenesulfonyl-4,5-dimethyl-o-phenylenediamines (**1**–**5**).

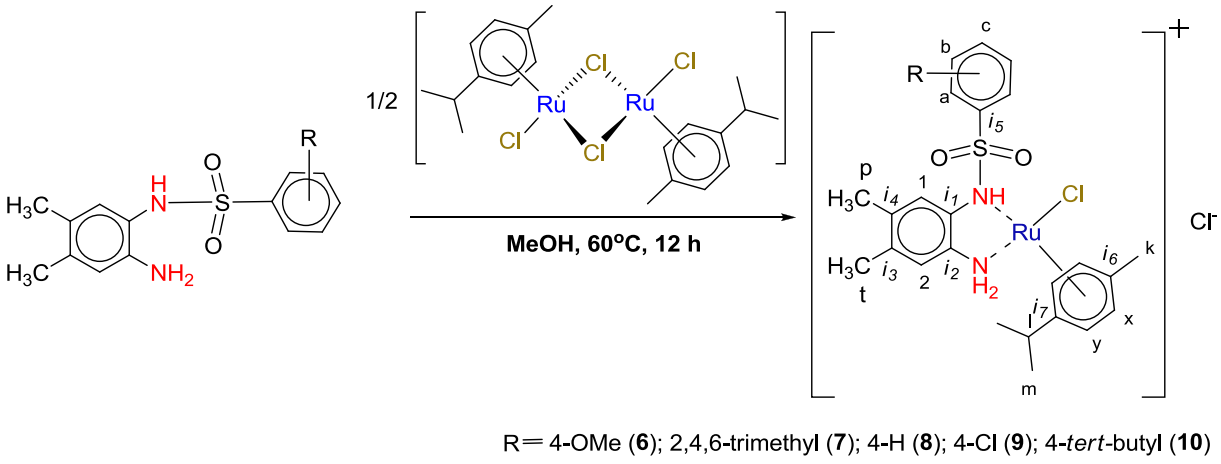


Fig. 2. Synthesis of the [(*p*-cymene)RuLCl]Cl complexes (**6**–**10**).

Table 1
Effect of various bases in the TH of acetophenone catalyzed by **9** (0.2 mol-%) in 2-propanol at 82 °C.

Entry	Catalyst	Base	(mmol)	Yield (%)[h]							TOF[j] (h^{-1})
1	9	NaOH	(1)	14[a]	30[b]	51[c]	60[d]	68[e]	72[f]	75[g]	420[a]
2	9	KOH	(1)	21[a]	41[b]	59[c]	67[d]	75[e]	77[f]	82[g]	630[a]
3	9	$KOBu^t$	(1)	9[a]	16[b]	27[c]	36[d]	41[e]	47[f]	52[g]	270[a]
4	9	K_2CO_3	(1)	7[a]	12[b]	19[c]	29[d]	36[e]	41[f]	45[g]	210[a]
5	9	KOH	(0.1)	4[a]	7[b]	11[c]	14[d]	17[e]	21[f]	23[g]	120[a]
6	9	absence of base		<5[g]							n.c.[g]
7	$[RuCl_2(p\text{-simen})]_2$	KOH	(1)	14[a]	16[b]	21[c]	27[d]	35[e]	40[f]	45[g]	420[a]
8	absence of catalyst	KOH	(10)	11[d], 16[g]							11[d]

Reaction conditions: 5.0 mmol of acetophenone, 1 mmol of base, 0.01 mmol Ru(II) complexes, 2-propanol (6 mL); all reactions were monitored by TLC and GC; temperature 80 °C.
[a] 10 min.
[b] 20 min.
[c] 40 min.
[d] 60 min.
[e] 80 min.
[f] 100 min.
[g] 120 min.
[h] GC yields, yields are based on phenyl ethanol, [1]TON = moles of product/moles of the catalyst.
[j] TOF = moles of product/(moles of the catalyst)x(hour), n. c.: not calculated.

4-chloroacetophenone, respectively.

Furthermore, the catalytic efficiency of the best catalyst **9** was also tested in the TH of 4-bromoacetophenone, 4-floroacetophenone, 2,4,6-trimethylacetophenone (as steric ketones) and cyclohexanone (as aliphatic ketones). In the presence of 4-bromoacetophenone, 4-floroacetophenone, 2,4,6-trimethylacetophenone and cyclohexanone conversion rates of 100%, 100%, 19% and 76% respectively were achieved in 100 min with the best catalyst **9** (Table 2).

Within these frameworks, we also investigated the 4-chloroacetophenone, 4-methylacetophenone and acetophenone TH at a (S/C/base) molar ratio of 10:0.01:1 (Table 3). The catalytic experiments showed that the complexes **8** and **9** are highly efficient. The highest measured TOFs were **1534** and **1731** h^{-1} for complexes **8** and **9** in the TH of 4-chloroacetophenone at 10 min, respectively. When the TH of Ru(II) arene complexes was examined in the literature, it is seen that the catalysts used in this study had a good efficiency in the TH [25–30].

3. Experimental

3.1. Materials and methods

All reagents and solvents were obtained from commercial suppliers and used without any additional purification. The NMR spectra were recorded at 297 K on a Bruker 400 NMR spectrometer at 400 MHz (^1H) and 100.56 MHz (^{13}C). The NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (*J*-values) are given in hertz. NMR multiplicities are abbreviated as follows: br = broad, s = singlet, d = doublet, t = triplet, m = multiplet signal. The C, H, and N analyses were performed using a Truspec MICRO (LECO) instrument. Infrared spectra were measured with a Perkin–Elmer Spectrum 400 FTIR system and recorded using a universal ATR sampling accessory within the range 550–4000 cm^{-1}. Melting points were determined in open capillary tubes on a digital Electrothermal 9100 melting point apparatus. GC measurements for catalytic experiments were performed using a Younglin Acme 6100 GC instrument with a flame ionization detector and an Optima 5MS capillary column (The GC parameters were as follows: Oven: 80 °C (isothermal); Carrier gas: H_2 (Split ratio 15:1); Flow rate: 4 mL/min; Injector port temperature: 220 °C; Detector temperature: 280 °C; Injection volume: 6.0 μL). The peak areas were founded with the internal standard technique using GC.

3.1.1. General procedure for the synthesis of ligands (L), 1-5 *N*-arenesulfonyl-4,5-dimethyl-o-phenylenediamines were

Table 2
Catalytic activity as shown by the % conversion vs. time for the TH of acetophenone, 4-methylacetophenone, 4-chloroacetophenone catalyzed by compounds **6**–**10** in 2-propanol. Conditions: *p*-substituted acetophenone/Ru/KOH, 5:0.01:1; T = 82 °C.

Entry	Catalyst	Substrate	Yield (%)[h]							TOF[j] (h^{-1})
1	6	Acetophenone	23[a]	40[b]	45[c]	56[d]	63[e]	67[f]	78[g]	685[a]
2	7		27[a]	33[b]	47[c]	54[d]	57[e]	63[f]	75[g]	798[a]
3	8		21[a]	41[b]	51[c]	65[d]	74[e]	78[f]	80[g]	616[a]
4	9		21[a]	41[b]	59[c]	67[d]	75[e]	77[f]	82[g]	635[a]
5	10		18[a]	37[b]	43[c]	55[d]	61[e]	67[f]	68[g]	525[a]
6	6	4-methylacetophenone	3[a]	6[b]	18[c]	35[d]	38[e]	43[f]	48[g]	98[a]
7	7		4[a]	7[b]	22[c]	30[d]	34[e]	40[f]	48[g]	128[a]
8	8		5[a]	10[b]	26[c]	36[d]	37[e]	43[f]	50[g]	165[a]
9	9		7[a]	12[b]	21[c]	30[d]	37[e]	42[f]	53[g]	210[a]
10	10		6[a]	9[b]	24[c]	33[d]	38[e]	44[f]	49[g]	179[a]
11	6	4-chloroacetophenone	45[a]	56[b]	68[c]	72[d]	82[e]	87[f]	93[g]	1340[a]
12	7		40[a]	54[b]	69[c]	76[d]	80[e]	84[f]	88[g]	1210[a]
13	8		43[a]	69[b]	75[c]	84[d]	89[e]	94[f]	97[g]	1307[a]
14	9		46[a]	59[b]	71[c]	87[d]	95[e]	98[f]	100[g]	1390[a]
15	10		41[a]	53[b]	63[c]	72[d]	76[e]	82[f]	88[g]	1222[a]
16	9	4-bromoacetophenone	49[a]	66[b]	80[c]	91[d]	98[e]	100[f]	100[g]	1470[a]
17	9	4-floroacetophenone	52[a]	69[b]	81[c]	92[d]	99[e]	100[f]	100[g]	1560[a]
18	9	2,4,6-trimethylacetophenone	<3[a]	<3[b]	8[c]	13[d]	17[e]	19[f]	21[g]	n.c.
19	9	Cyclohexanone	25[a]	36[b]	50[c]	61[d]	69[e]	76[f]	81[g]	750[a]

Reaction conditions: 5.0 mmol of substrate, 1.0 mmol of KOH, 0.01 mmol Ru(II) complexes, 2-propanol (6 mL); all reactions were monitored by TLC and GC; temperature 80 °C.
[a] 10 min.
[b] 20 min.
[c] 40 min.
[d] 60 min.
[e] 80 min.
[f] 100 min.
[g] 120 min.
[h] GC yields, the yields obtained were related to the residual unreacted acetophenone and formed phenyl ethanol, [1]TON = moles of product/moles of the catalyst.
[j] TOF = moles of product/(moles of the catalyst)x(hour). n. c. = not calculated.

Table 3
Catalytic activity as shown by the % conversion vs. time for the TH of (**a**) acetophenone, (**b**) 4-methylacetophenone, (**c**) 4-chloroacetophenone catalyzed by compounds **6**–**10** in 2-propanol. Conditions: *p*-substituted acetophenone/Ru/KOH, 10:0.01:1; T = 82 °C.

Entry	Catalyst	Substrate	Yield (%)[h]							TOF[j] (h^{-1})
1	6	Acetophenone	24[a]	32[b]	45[c]	52[d]	57[e]	58[f]	65[g]	1422[a]
2	7		14[a]	33[b]	44[c]	51[d]	56[e]	60[f]	66[g]	834[a]
3	8		20[a]	29[b]	40[c]	50[d]	58[e]	62[f]	69[g]	1213[a]
4	9		27[a]	41[b]	52[c]	61[d]	65[e]	67[f]	70[g]	1617[a]
5	10		21[a]	30[b]	39[c]	42[d]	53[e]	59[f]	64[g]	1233[a]
6	6	4-methylacetophenone	4[a]	9[b]	18[c]	23[d]	40[e]	45[f]	47[g]	238[a]
7	7		4[a]	8[b]	18[c]	26[d]	38[e]	42[f]	45[g]	245[a]
8	8		4[a]	9[b]	22[c]	29[d]	35[e]	42[f]	48[g]	218[a]
9	9		5[a]	11[b]	24[c]	29[d]	37[e]	45[f]	49[g]	296[a]
10	10		4[a]	10[b]	17[c]	28[d]	36[e]	40[f]	45[g]	271[a]
11	6	4-chloroacetophenone	28[a]	51[b]	66[c]	78[d]	85[e]	87[f]	88[g]	1657[a]
12	7		21[a]	31[b]	51[c]	58[d]	67[e]	71[f]	80[g]	1276[a]
13	8		26[a]	30[b]	45[c]	72[d]	79[e]	90[f]	91[g]	1534[a]
14	9		29[a]	45[b]	60[c]	70[d]	77[e]	85[f]	94[g]	1731[a]
15	10		28[a]	40[b]	59[c]	77[d]	80[e]	84[f]	86[g]	1659[a]

Reaction conditions: 10.0 mmol of substrate, 1.0 mmol of KOH, 0.01 mmol Ru(II) complexes, 2-propanol (6 mL); all reactions were monitored by TLC and GC; temperature 80 °C.
[a] 10 min.
[b] 20 min.
[c] 40 min.
[d] 60 min.
[e] 80 min.
[f] 100 min.
[g] 120 min.
[h] GC yields, the yields obtained were related to the residual unreacted acetophenone formed phenyl ethanol, [1]TON = moles of product/moles of the catalyst.
[j] TOF = moles of product/(moles of the catalyst)x(hour).

prepared in accordance to the published experimental procedure [16,23,24].

A solution of benzenesulfonylchlorides (5 mmol) in THF (10 ml) was added drop wise to a solution of triethylamine (10 mmol) with a dropping funnel in THF (5 ml) in a Schlenk tube. After a few minutes, a THF (5 ml) solution of 4,5-dimethyl-o-phenylenediamine (5 mmol) was added slowly at ambient temperature, and the reaction continued for a period of 12 h. A solid filtrate was left as a by-product. The volatiles were removed under reduced pressure (Fig. 1). The residue was dissolved in DCM (20 ml) and washed with H_2O (3 × 50 ml) at room temperature. The organic layer was separated and dried over anhydrous $MgSO_4$, filtered, and concentrated to half of its volume under reduced pressure. An analytically pure sample can be isolated by recrystallization from chloroform/

diethyl ether (12 ml 1:5, v/v).

3.1.1.1. Data for the ligands 1-5

3.1.1.1.1. For N-4-methoxybenzenesulfonyl-4,5-dimethyl-o-phenylenediamine (1). Color: Light Brown. Yield: 84%. Mp: 144 °C. ^{1}H-NMR ($CDCl_3$, δ ppm): 1.96 (s, 3H, -H_t), 2.11 (s, 3H, -H_p), 3.85 (s, 3H, -OCH_3), 6.33 (s, 1H, -H_2), 6.53 (s, 1H, -H_1), 6.91 (d, 2H, J = 8 Hz, -H_b), 7.68 (d, 2H, J = 8 Hz, -H_a). ^{13}C-NMR ($CDCl_3$, ppm): 18.6 (-CH_3 *(p)*), 19.5 (-CH_3 (t)), 55.6 (-OCH_3), 114.0 (-C_b), 118.6 (-C_2), 119.1 (-C_1), 127.0 (-C_{i3}), 129.5 (-C_{i4}), 129.7 (-C_a), 130.9 (-C_{i5}), 137.3 (-C_{i1}), 141.7 (-C_{i2}), 163.0 (-C_c). IR (cm^{-1}): 3419 (-NH_2), 3339 (-NH), 3092, 3062, 3029, 2984, 2949, 1619, 1593, 1575, 1512, 1494, 1456, 1442, 1417, 1391, 1374, 1322 (ν_{as}-SO_2), 1306, 1295, 1248, 1224, 1175, 1153 (ν_s-SO_2), 1106, 1090, 1012, 910, 881, 863, 837, 801, 761, 743, 717, 662, 629, 621, 579, 567, 555 (**Δ**-SO_2), 508, 500, 491, 483, 464, 458. Anal. Calcd. For: [$C_{15}H_{18}N_2O_3S$] C: 58.80, H: 5.92, N: 15.67, S: 10.47. Found: C: 58.88, H: 5.99, N: 15.56, S: 10.55.

3.1.1.1.2. For N-2,4,6-trimethylbenzenesulfonyl-4,5-dimethyl-o-phenylenediamine (2). Color: Light Brown. Yield: 83%. Mp: 95 °C. ^{1}H-NMR ($CDCl_3$, δ ppm): 1.90 (s, 3H, -H_t), 2.09 (s, 3H, -H_p), 2.30 (s, 3H, *p*-CH_3), 2.47 (s, 6H, *o*-CH_3), 6.15 (s, 1H, -H_2), 6.52 (s, 1H, -H_1), 6.92 (s, 2H, -H_b). ^{13}C-NMR ($CDCl_3$, ppm): 18.5 (-CH_3*(p)*), 19.5 (-CH_3 (t)), 21.0 (*p*-CH_3), 23.1 (*o*-CH_3), 118.5 (-C_2), 118.7 (-C_1), 126.9 (-C_{i3}), 129.5 (-C_{i4}), 131.8 (-C_b), 133.7 (-C_{i5}), 137.4 (-C_{i1}), 139.5 (-C_a), 142.1 (-C_{i2}), 142.4 (-C_c). IR (cm^{-1}): 3417 (-NH_2), 3334 (-NH), 3020, 2973, 2938, 2860, 1623, 1601, 1563, 1510, 1455, 1399, 1380, 1365, 1308 (ν_{as}-SO_2), 1267, 1221, 1186, 1146 (ν_s-SO_2), 1087, 1057, 1033, 1003, 965, 910, 855, 749, 728, 679, 648, 621, 577, 535, 512 (**Δ**-SO_2), 470, 457. Anal. Calcd. For: [$C_{17}H_{22}N_2O_2S$] C: 64.12, H: 6.96, N: 8.80, S: 10.07. Found: C: 64.21, H: 7.08, N: 8.84, S: 10.01.

3.1.1.1.3. For N-benzenesulfonyl-4,5-dimethyl-o-phenylenediamine (3). Color: Light Pink. Yield: 82%. Mp: 117 °C. ^{1}H-NMR ($CDCl_3$, δ ppm): 1.93 (s, 3H, -H_t), 2.10 (s, 3H, -H_p), 6.29 (s, 1H, -H_2), 6.56 (s, 1H, -H_1), 7.41–7.78 (m, 5H, -$H_{a\text{-}c}$). ^{13}C-NMR ($CDCl_3$, ppm): 18.5 (-CH_3 *(p)*), 19.5 (-CH_3 (t)), 118.9 (-C_2), 126.0 (-C_1), 127.5 (-C_a), 127.6 (-C_{i3}), 128.9 (-C_{i4}), 129.5 (-C_b), 132.9 (-C_c), 133.0 (-C_{i1}), 137.5 (-C_{i5}), 139.2 (-C_{i2}). IR (cm^{-1}): 3414 (-NH_2), 3335 (-NH), 3031, 2980, 2950, 2916, 2864, 1616, 1604, 1584, 1515, 1473, 1447, 1391, 1373, 1325 (ν_{as}-SO_2), 1309, 1293, 1270, 1223, 1197, 1164, 1155 (ν_s-SO_2), 1123, 1089, 1070, 1033, 1025, 1015, 998, 917, 900, 883, 862, 777, 758, 720, 690, 623, 612, 590, 574, 559 (**Δ**-SO_2), 534, 513, 482, 460. Anal. Calcd. For: [$C_{14}H_{16}N_2O_2S$] C: 60.85, H: 5.84, N: 10.14, S: 11.60. Found: C: 60.72, H: 5.92, N: 10.08, S: 11.52.

3.1.1.1.4. For N-4-chlorobenzenesulfonyl-4,5-dimethyl-o-phenylenediamine (4). Color: Light Pink. Yield: 83%. Mp: 120 °C. ^{1}H-NMR ($CDCl_3$, δ ppm): 1.97 (s, 3H, -H_t), 2.12 (s, 3H, -H_p), 6.31 (s, 1H, -H_2), 6.56 (s, 1H, -H_1), 7.42 (d, 2H, J = 8 Hz, -H_b), 7.69 (d, 2H, J = 8 Hz, -H_a). ^{13}C-NMR ($CDCl_3$, ppm): 18.6 (-CH_3 *(p)*), 19.5 (-CH_3 (t)), 118.8 (-C_2), 119.0 (-C_1), 127.6 (-C_a), 129.0 (-C_{i3}), 129.1 (-C_{i4}), 129.3 (-C_b), 137.4 (-C_{i1}), 137.8 (-C_c), 139.4 (-C_{i5}), 141.1 (-C_{i2}). IR (cm^{-1}): 3470 (-NH_2), 3383 (-NH), 3093, 3021, 2970, 2921, 2859, 1626, 1575, 1510, 1475, 1456, 1393, 1314 (ν_{as}-SO_2), 1280, 1218, 1160 (ν_s-SO_2), 1090, 1033, 1005, 916, 881, 855, 822, 752, 706, 648, 626, 604, 583 (**Δ**-SO_2), 539, 481. Anal. Calcd. For: [$C_{14}H_{15}N_2O_2S$] C: 54.10, H: 4.86, N: 9.01, S: 10.32. Found: C: 54.02, H: 4.93, N: 9.15, S: 10.27.

3.1.1.1.5. For N-4-tert-butylbenzenesulfonyl-4,5-dimethyl-o-phenylenediamine (5). Color: Light Pink. Yield: 81%. Mp: 134 °C. ^{1}H-NMR ($CDCl_3$, δ ppm): 1.34 (s, 9H, –C(CH_3)$_3$), 1.91 (s, 3H, -H_t), 2.11 (s, 3H, -H_p), 6.19 (s, 1H, -H_2), 6.55 (s, 1H, -H_1), 7.46 (d, 2H, J = 8 Hz, -H_b), 7.68 (d, 2H, J = 8 Hz, -H_a). ^{13}C-NMR ($CDCl_3$, ppm): 18.5 (-CH_3 *(p)*), 19.5 (-CH_3 (t)), 31.1 (-C(CH_3)$_3$), 35.2 (-C(CH$_3$)$_3$), 118.7 (-C_2), 119.0 (-C_1), 125.8 (-C_b), 126.9 (-C_a), 127.5 (-C_{i3}), 129.5 (-C_{i4}), 136.0 (-C_{i1}), 137.4 (-C_{i5}), 141.7 (-C_{i2}), 156.8 (-C_c). IR (cm^{-1}): 3425 (-NH_2), 3342 (-NH), 3073, 2954, 2907, 2867, 1595, 1514, 1506, 1479, 1463, 1456, 1395, 1363, 1325 (ν_{as}-SO_2), 1309, 1293, 1267, 1223, 1195, 1161 (ν_s-SO_2), 1111, 1086, 1016, 1005, 918, 883, 859, 842, 832, 754, 732, 682, 666, 624, 571 (**Δ**-SO_2), 555, 537, 521, 495, 476, 467, 457. Anal. Calcd. For: [$C_{18}H_{24}N_2O_2S$] C: 65.03, H: 7.28, N: 8.43, S: 9.64. Found: C: 64.93, H: 7.39, N: 8.37, S: 9.77.

3.1.2. General procedure for the synthesis of [(p-cymene)RuLCl]Cl, 6-10

A solution of **1**–**5** (0.50 mmol) in methyl alcohol (5 ml) was added to a solution of [$RuCl_2$(*p-cymene*)]$_2$ (0.25 mmol) in methyl alcohol (5 ml) in a Schlenk tube. The mixture was stirred for 12 h with a magnetic stirrer. After completion of the reaction time, the volatiles were removed under reduced pressure. The residue was washed with diethyl ether (20 ml) and dried under vacuum. The desired products were recrystallized from MeOH to give black or dark green-colored microcrystals (Fig. 2). The synthesized ruthenium(II) arene complexes are highly soluble in polar organic solvents such as chloroform, dichloromethane, DMSO and DMF and they are almost insoluble in diethyl ether and petroleum ether. The analytical data (C, H, N and S) are in good agreement with the compositions proposed for all the complexes.

3.1.2.1. For {[N-4-methoxybenzenesulfonyl-4,5-dimethyl-o-phenylenediamine]-(p-cymene)-di-chloro-ruthenium(II)} (6). Color: Black. Yield: 86%. Mp: 165 °C. ^{1}H-NMR ($CDCl_3$, δ ppm): 1.28 (d, 6H, J = 8 Hz, -H_m), 2.05 (s, 3H, -H_t), 2.15 (s, 6H, -H_p, -H_k), 2.91 (m, 1H, -H_l), 3.85 (s, 3H, -OCH_3), 5.35 (d, 2H, J = 4 Hz, -H_y), 5.47 (d, 2H, J = 4 Hz, -H_x), 6.74–8.07 (6H, -$H_{1,2}$, -$H_{a,b}$). ^{13}C-NMR ($CDCl_3$, ppm): 18.9 (-CH_3 *(p)*, -CH_3 *(k)*), 19.3 (-CH_3 (t)), 22.2 (-CH(CH_3)$_2$), 30.7 (-CH(CH$_3$)$_2$), 55.7 (-OCH$_3$), 80.6, 81.3, 96.8, 101.2, 114.1 (-C_b), 116.4 (-C_2), 119.1 (-C_1), 127.2 (-C_{i3}), 128.9 (-C_{i4}), 129.8 (-C_a), 130.8 (-C_{i5}), 135.9 (-C_{i1}), 141.4 (-C_{i2}), 163.1 (-C_c). IR (cm^{-1}): 3243 (-NH_2), 3151 (-NH), 3055, 2973, 2945, 2869, 1688, 1649, 1594, 1580, 1497, 1470, 1456, 1415, 1386, 1300 (ν_{as}-SO_2), 1255, 1180, 1151 (ν_s-SO_2), 1087, 1058, 1022, 1005, 901, 877, 834, 802, 780, 716, 667, 628, 608, 558 (**Δ**-SO_2). Anal. Calcd. For: C: 49.02, H: 5.27, N: 4.57, S: 5.23. Found: C: 49.11, H: 5.33, N: 4.50, S: 5.21.

3.1.2.2. For {[N-2,4,6-trimethylbenzenesulfonyl-4,5-dimethyl-o-phenylenediamine]-(p-cymene)-di-chloro-ruthenium(II)} (7). Color: Dark Green. Yield: 87%. Mp: 178 °C.^{1}H-NMR (DMSO, δ ppm): 1.18 (d, 6H, J = 8 Hz, -H_m), 1.95 (s, 3H, -H_t), 2.08 (s, 6H, -H_p, -H_k), 2.23 (s, 3H, *p*-CH_3), 2.41 (s, 3H, *o*-CH_3), 2.91 (m, 1H, -H_l), 5.77 (d, 2H, J = 4 Hz, -H_y), 5.81 (d, 2H, J = 4 Hz, -H_x), 6.46 (s, 1H, -H_2), 6.74 (s, 1H, -H_1), 6.98 (s, 2H, -H_b). ^{13}C-NMR (DMSO, ppm): 23.1 (-CH_3 *(p)*, -CH_3 *(k)*), 23.8 (-CH_3 (t)), 25.6 (*p*-CH_3), 26.7 (*o*-CH_3, –CH(CH_3)$_2$), 35.2 (-CH(CH$_3$)$_2$), 90.7, 91.6, 105.3, 111.7, 121.6 (-C_2), 128.1 (-C_1), 130.2 (-C_{i3}), 135 (-C_{i4}), 135.9 (-C_b), 136.7 (-C_{i5}), 136.8 (-C_{i1}), 137.0 (-C_a), 144.0 (-C_{i2}), 155.3 (-C_c). IR (cm^{-1}): 3253 (-NH_2), 3200 (-NH), 3050, 2965, 2872, 1691, 1646, 1603, 1564, 1514, 1506, 1471, 1455, 1403, 1386, 1323 (ν_{as}-SO_2), 1263, 1223, 1187, 1150 (ν_s-SO_2), 1087, 1055, 1032, 1013, 966, 878, 852, 804, 703, 655, 587, 573, 528 (**Δ**-SO_2), 457. Anal. Calcd. For: C: 51.92, H: 5.81, N: 4.48, S: 5.13. Found: C: 51.99, H: 5.75, N: 4.43, S: 5.18.

3.1.2.3. For {[N-benzenesulfonyl-4,5-dimethyl-o-phenylenediamine]-(p-cymene)-di-chloro-ruthenium(II)} (8). Color: Dark Green. Yield: 86%. Mp: 137 °C.^{1}H-NMR ($CDCl_3$, δ ppm): 1.28 (d, 6H, J = 8 Hz, -H_m), 2.03 (s, 3H, -H_t), 2.15 (s, 6H, -H_p, -H_k), 2.91 (m, 1H, -H_l), 5.34 (d, 2H, J = 4 Hz, -H_y), 5.48 (d, 2H, J = 4 Hz, -H_x), 6.69 (s, 1H, -H_2), 6.99 (s, 1H, -H_1), 7.35–8.14 (m, 5H, -$H_{a\text{-}c}$). ^{13}C-NMR ($CDCl_3$, ppm): 18.9 (-CH_3 *(p)*, -CH_3 *(k)*), 19.3 (-CH_3 (t)), 22.2 (-CH(CH_3)$_2$), 30.7 (-CH(CH$_3$)$_2$), 80.6, 81.3, 96.8, 101.3, 124.4 (-C_2), 126.0 (-C_1), 126.5 (-C_a), 127.3 (-C_{i3}), 127.5 (-C_{i4}), 127.9 (-C_b), 128.6 (-C_c), 128.9 (-C_{i1}), 131.8 (-C_{i5}), 133.1 (-C_{i2}). IR (cm^{-1}): 3280 (-NH_2), 3212 (-NH), 3058, 2964, 2925, 2872, 1687, 1646, 1608, 1558, 1512, 1471, 1446, 1387, 1326 (ν_{as}-SO_2), 1310,

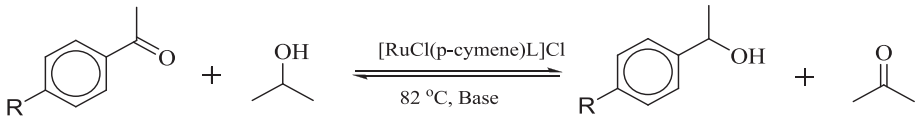


Fig. 3. TH of acetophenone derivatives to corresponding alcohols with [RuCl(p-cymene)L]Cl.

1289, 1263, 1158 (ν_s-SO_2), 1087, 1058, 1033, 1018, 904, 876, 846, 804, 756, 723, 689, 667, 611, 580, 544 (Δ-SO_2), 480. Anal. Calcd. For: C: 49.48, H: 5.19, N: 4.81, S: 5.50. Found: C: 49.53, H: 5.25, N: 4.73, S: 5.61.

3.1.2.4. For {[N-4-chlorobenzenesulfonyl-4,5-dimethyl-o-phenylenediamine]-(p-cymene)-di-chloro-ruthenium(II)} (9). Color: Dark Green. Yield: 87%. Mp: 171 °C. ^{1}H-NMR ($CDCl_3$, δ ppm): 1.28 (d, 6H, J = 8 Hz, -H_m), 2.26 (s, 3H, -H_t), 2.18 (s, 6H, -H_p, -H_k), 2.91 (m, 1H, -H_l), 5.34 (d, 2H, J = 4 Hz, -H_y), 5.48 (d, 2H, J = 4 Hz, -H_x), 6.88–8.09 (7H, -$H_{a\text{-}c,}$ -$H_{1,2}$). ^{13}C-NMR ($CDCl_3$, ppm): 18.9 (-CH_3 *(p)*, -CH_3 *(k)*), 19.4 (-CH_3 (t)), 22.1 (-CH(CH_3)$_2$), 30.6 (-CH(CH_3)$_2$), 80.6, 81.3, 96.8, 101.3, 121.8 (-C_2), 124.3 (-C_1), 126.6 (-C_a), 128.2 (-C_{i3}), 128.9 (-C_{i4}), 129.4 (-C_b), 129.5 (-C_{i1}), 130.2 (-C_c), 135.3 (-C_{i5}), 139.6 (-C_{i2}). IR (cm^{-1}): 3296 (-NH_2), 3218 (-NH), 3057, 3035, 2964, 2924, 2872, 1607, 1585, 1515, 1474, 1455, 1390, 1327 (ν_{as}-SO_2), 1293, 1280, 1264, 1161 (ν_s-SO_2), 1086, 1058, 1033, 1013, 908, 877, 827, 805, 754, 706, 614, 576, 543 (Δ-SO_2), 480. Anal. Calcd. For: C: 46.72, H: 4.74, N: 4.54, S: 5.20. Found: C: 46.85, H: 4.69, N: 4.43, S: 5.29.

3.1.2.5. For {[N-4-tert-butylbenzenesulfonyl-4,5-dimethyl-o-phenylenediamine]-(p-cymene)-di-chloro-ruthenium(II)} (10). Color: Black. Yield: 81%. Mp: 186 °C. ^{1}H-NMR ($CDCl_3$, δ ppm): 1.28 (d, 6H, J = 8 Hz, -H_m), 1.34 (s, 9H, –C(CH_3)$_3$), 2.16 (s, 6H, -H_p, -H_k), 2.25 (s, 3H, -H_t), 2.92 (m, 1H, -H_l), 5.35 (d, 2H, J = 4 Hz, -H_y), 5.48 (d, 2H, J = 4 Hz, -H_x), 6.70–8.05 (6H, -$H_{a,b,1,2}$). ^{13}C-NMR ($CDCl_3$, ppm): 18.9 (-CH_3 *(p)*, -CH_3 *(k)*), 19.3 (-CH_3 (t)), 22.1 (-CH(CH_3)$_2$), 30.6 (-CH(CH_3)$_2$), 31.0 (-C(CH_3)$_3$), 31.1 (-C(CH_3)$_3$), 80.6, 81.3, 96.8, 101.3, 124.3 (-C_2), 125.0 (-C_1), 126.2 (-C_b), 126.4 (-C_a), 127.2 (-C_{i3}), 127.4 (-C_{i4}), 128.4 (-C_{i1}), 129.0 (-C_{i5}), 138.0 (-C_{i2}), 152.7 (-C_c). IR (cm^{-1}): 3278 (-NH_2), 3205 (-NH), 3049, 2962, 2928, 2870, 1596, 1514, 1506, 1496, 1463, 1390, 1363, 1324 (ν_{as}-SO_2), 1290, 1264, 1199, 1161 (ν_s-SO_2), 1111, 1084, 1056, 1033, 1007, 902, 877, 835, 804, 754, 734, 719, 628, 569, 548 (Δ-SO_2), 514, 482, 460. Anal. Calcd. For: C: 52.66, H: 6.00, N: 4.39, S: 5.02. Found: C: 52.71, H: 6.05, N: 4.45, S: 4.97.

3.1.3. General procedure for the transfer hydrogenation reaction

In a typical experiment, under an argon atmosphere, the ruthenium(II) arene complexes (0.01 mmol) and acetophenone (5 mmol) were placed in a Schlenk flask and 6 ml 2-propanol was added to the mixture, which was then stirred for 15 min at ambient temperature. Then 1 mmol base was added to the mixture and it was heated at 82 °C under reflux for the desired period of time. After the desired reaction time, the sample was diluted with diethyl ether (5 ml) and filtered from a mini-column. The purity of the compounds was checked by GC. The yields obtained were related to the residual unreacted acetophenone and (Fig. 3).

4. Conclusions

Herein, a series of *N*-coordinate complexes precursors which bearing the sulfonamide moiety (**1**–**5**) and their half-sandwich ruthenium(II) complexes were synthesized and characterized. Also, the catalytic activities of [(*p*-cymene)RuLCl]Cl (**6**–**10**) complexes were examined in the TH of ketones in the presences of base in 2-propanol (as hydrogen donor). The efficiency of the catalyst seems to depend not only on the ligands of the complex but also on the substituents of the aromatic ketones. Within these frameworks, the best result was obtained in the presence of the –Cl substituent at the *para* position of the sulfonamide aryl group. Additionally, the electron-withdrawing group (-Cl, -F, -Br) introduced into the *para* position of the acetophenone increased the yield, whereas the electron-donating group (-CH_3) at the *para* position of the acetophenone decreased the yield. Moreover, when 2,4,6-trimethylacetophenone was used as a substrate, a constant decrease in the catalytic yield was observed, which was probably due to steric effects. Furthermore, the best catalyst **9** was observed as effective catalyst for TH of aliphatic ketones (cyclohexanone). So that this type ruthenium(II) complexes were determined as active catalysts in the TH of aliphatic ketones. The catalytic activity for the TH of ketones increases in the order **10** < **7** < **6** < **8** < **9**.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2015.06.082.

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