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Synthesis of ruthenium(II) complexes derived from reduced imine ligands: As catalysts for transfer hydrogenation of ketones

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ABSTRACT

N-[2-(benzylamino)phenyl]benzenesulfonamide derivatives (**1**–**6**) were successfully synthesized by the reaction of imine ligands derived from various *N*-(2-aminophenyl)benzenesulfonamides and $NaBH_4$. Then, a series of *N*-coordinate Ru(II) arene complexes **7**–**12** were prepared from the reaction of $[RuCl_2(p\text{-}cymene)]_2$ with **1**–**6**. The synthesized compounds were characterized by different methods such as NMR, FT-IR, and elemental analysis. **7**–**12** were used as catalysts for the transfer hydrogenation (TH) of ketones. At the same time, the effect of various bases such as NaOH, KOH, $KOBu^t$ and Et_3N as organic base were investigated in TH of ketones by 2-propanol as the hydrogen source. **7**–**12** showed good catalytic activity and so the effects of the different groups were also examined.

1. Introduction

In general, sulfonamides are obtained from the reaction of sulfonyl chloride with primary or secondary amines in alkaline [1]. The sulfonamides and their derivatives have attracted the interest of many researchers due to their importance in the development of coordination chemistry, their application in medicinal chemistry, catalytic fields, etc. [2–18]. For example, metal complexes containing sulfonamide ligands have been used as catalysts in different organic reactions [19–26].

The transfer hydrogenation (TH) of ketones catalyzed by Ru(II) complexes bearing *N*-donor ligands has been attracting more and more attention from the catalysis community [27–38] since the success of Noyori's catalyst, bearing 1,2-diamine ligands [39]. After Noyori et al., researchers, many derivatives of Ru(II) complexes containing *N*-donor ligands have aimed to identify a good Ru(II) catalyst for the TH of ketones. Hereof, ligand groups which have Ru(II) complexes with unique catalytic activity are sulfonamides.

Otherwise, Schiff base and reduced Schiff base compounds are also receiving more and more attention in the fields of polymeric complexes, coordination chemistry, magnetic properties, optical property, thermal decomposition, medicinal chemistry, catalyst chemistry, etc. [40–69]. In addition, palladium complexes bearing diamine and diimine were used as catalyst for Suzuki Cross-Coupling [70]. Further, the TH of acetophenone was carried out by ruthenium(II) complexes of reduced Schiff base ligands. The Ru(II) complexes were found as active catalyst [71]. *N*-heterocyclic carbene (NHC) ligands derivatives from reduced Schiff base ligands have been synthesized. Then, a series of Ru(II) complexes were prepared with the NHC ligands. The complexes were used for the catalytic transfer hydrogenation of aromatic ketones, recently [72].

In this place, a series of neutral Ru(II) arene complexes derived from reduced imine ligands bearing aromatic sulfonamide were synthesized and characterized by various spectroscopic techniques. **7**–**12** were used as catalysts for the TH of *p*-substituent acetophenone derivative. The synthesis procedure of ligands **1**–**6** and complexes **7**–**12** are simple and does not require an inert atmosphere and it can be carried out in at mild-temperatures.

2. Experimental

2.1. Materials and methods

All reagents and solvents were obtained from commercial suppliers and used without any additional purification. 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 =

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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).

2.2. General procedure for the synthesis of 1–6

N-(2-aminophenyl)benzenesulfonamides and the Schiff base derivatives of those compounds were prepared in accordance with the published procedure [73a–c]. Solid sodium borohydride (0.2 mmol) was added slowly to a solution of *N*-[2-(benzylamino)phenyl]benzenesulfonamide derivatives (0.2 mmol) in methanol (10 ml). The solution was stirred at ambient temperature for a period of 12 h. The volatiles were removed under reduced pressure. 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. The solution was saturated with diethyl ether and left in the refrigerator for crystallization. Gradually, a microcrystalline product separated, which was filtered off, and dried *in vacuo* (Fig. 1).

2.2.1. Data for the 1–6

(**1**)-*N*-*[2-(benzylamino)-phenyl]benzenesulfonamide*

Color: light pink. Yield: 92%. Mp: 132–133 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 4.30 (s, 2H, –C*H*$_2$–), 6.36 (br. –N*H*–), 6.47–7.35 (9H, –*H*$_{1-4}$, –*H*$_{x-z}$), 7.46 (t, 2H, *J* = 8 Hz, –*H*$_b$), 7.59 (t, 2H, *J* = 8 Hz, –*H*$_c$), 7.78 (d, 2H, *J* = 8 Hz, –*H*$_a$). ^{13}C NMR ($CDCl_3$, ppm): 48.1 (–CH_2–), 112.8 (Ar. –*C*), 117.3 (Ar. –*C*), 120.6 (Ar. –*C*), 127.3 (Ar. –*C*), 127.4 (Ar. –*C*), 127.6 (Ar. –*C*), 128.6 (Ar. –*C*), 128.7 (Ar. –*C*), 129.0 (Ar. –*C*), 129.4 (Ar. –*C*), 133.1 (Ar. –*C*), 138.5 (Ar. –*C*), 139.0 (Ar. –*C*), 145.2 (Ar. –*C*). IR (cm^{-1}): 3426 (–N*H*–CH_2–), 3255 (–N*H*), 3055, 3027, 2988, 2969, 2902, 1602, 1585, 1515, 1494, 1469, 1453, 1447, 1436, 1394, 1366 (–SO_2), 1322, 1298, 1280, 1262, 1208, 1178, 1151 (SO_2), 1122, 1088, 1060, 1049, 1026, 996, 974, 941, 909, 880, 858, 834, 804, 779, 750, 736, 727, 712, 697, 685, 665, 635, 590, 564, 539, 500, 485, 458. *Anal.* Calc. for: C: 67.43, H: 5.36, N: 8.28, O: 9.46, S: 9.47. Found: C: 67.25, H: 5.16, N: 8.35, S: 9.60%.

(**2**)-*N*-*[2-(benzylamino)-4-methoxy-phenyl]benzenesulfonamide*

Color: light pink. Yield: 84%. Mp: 119–120 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 3.83 (s, 3H, –OC*H*$_3$), 4.24 (s, 2H, –C*H*$_2$–) 6.33–7.80 (15H, –N*H*– *H*$_{1-4}$, –*H*$_{a-c}$ and –*H*$_{x-y}$). ^{13}C NMR ($CDCl_3$, ppm): 47.26 (–CH_2–), 55.2 (–OCH_3), 112.3 (Ar. –*C*), 114.0 (Ar. –*C*), 116.7 (Ar. –*C*), 120.2 (Ar. –*C*), 127.5 (Ar. –*C*), 126.6 (Ar. –*C*), 128.5 (Ar. –*C*), 128.7 (Ar. –*C*), 128.9 (Ar. –*C*), 129.3 (Ar. –*C*), 130.7 (Ar. –*C*), 133.0 (Ar. –*C*), 138.9 (Ar. –*C*), 145.6 (Ar. –*C*). IR (cm^{-1}): 3434 (–N*H*–CH_2–), 3242 (–N*H*), 3002, 2909, 2837, 1603, 1583, 1510, 1467, 1445, 1401, 1365 (–SO_2), 1323, 1286, 1245, 1207, 1178, 1150 (–SO_2), 1092, 1071, 1047, 1029, 992, 989, 913, 832, 807, 753, 740, 730, 711, 686, 632, 595, 558, 535, 462. *Anal.* Calc. for: C: 65.20, H: 5.47, N: 7.60, O: 13.03, S: 8.70. Found: C: 65.12, H: 5.60, N:7.52, S:8.63%.

(**3**)-*N*-*[2-(benzylamino)-4-methyl-phenyl]benzenesulfonamide*

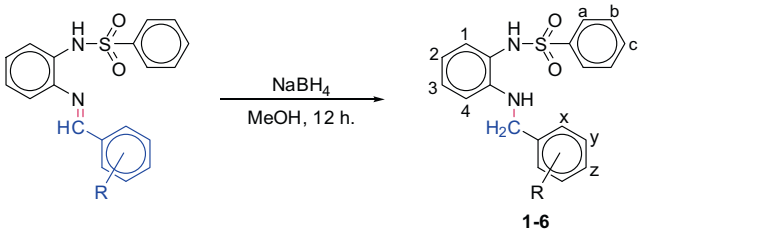
Color: light pink. Yield: 80%. Mp: 162–163 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 2.35 (s, 3H, –C*H*$_3$), 4.25 (s, 2H, –C*H*$_2$–), 6.54–7.80 (15H, –N*H*–, *H*$_{1-4}$, –*H*$_{a-c}$, and –*H*$_{x-y}$). ^{13}C NMR ($CDCl_3$, ppm): 21.1 (–CH_3), 48.22 (–CH_2–), 118.0 (Ar. –*C*), 127.3 (Ar. –*C*), 127.6 (Ar. –*C*), 128.5 (Ar. –*C*), 129.0 (Ar. –*C*), 129.2 (Ar. –*C*), 129.3 (Ar. –*C*), 129.8 (Ar. –*C*), 130.0 (Ar. –*C*), 131.9 (Ar. –*C*), 132.7 (Ar. –*C*), 133.1 (Ar. –*C*). IR (cm^{-1}): 3441 (–N*H*–CH_2–), 3205 (–N*H*), 3073, 3045, 3017, 2932, 2916, 2856, 2783, 1600, 1581, 1514, 1482, 1467, 1448, 1436, 1406, 1362 (–SO_2), 1326, 1317, 1300, 1282, 1252, 1205, 1179, 1162 (–SO_2), 1146, 1128, 1113, 1091, 1072, 1048, 1020, 999, 992, 940, 920, 833, 797, 779, 758, 747, 730, 711, 665, 668, 647, 639, 596, 561, 533, 517, 506, 474. *Anal.* Calc. for: C: 68.16, H: 5.72, N: 7.95, O: 9.08, S: 9.10. Found: C: 68.22, H: 5.62, N: 7.99, S: 9.02%.

(**4**)-*N*-*[2-(benzylamino)-2,4-di-methyl-phenyl]benzenesulfonamide*

Color: dark orange. Yield: 78%. Mp: 110–111 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 2.32 (s, 3H, –(CH_3)$_p$), 2.34 (s, 3H, –(CH_3)$_o$), 4.19 (s, 2H, –C*H*$_2$–), 4.75 and 6.08 (br. 2H, –N*H*–), 6.46–7.78 (12H, *H*$_{1-4}$, –*H*$_{a-c}$, and –*H*$_{x-y}$). ^{13}C NMR ($CDCl_3$, ppm): 18.9 (–(CH_3)$_p$), 21.0 (–(CH_3)$_o$), 45.7 (–CH_2–), 112.0 (Ar. –*C*), 116.6 (Ar. –*C*), 120.1 (Ar. –*C*), 126.8 (Ar. –*C*), 127.6 (Ar. –*C*), 128.0 (Ar. –*C*), 128.7 (Ar. –*C*), 129.0 (Ar. –*C*), 129.5 (Ar. –*C*), 131.3 (Ar. –*C*), 133.1 (Ar. –*C*), 133.4 (Ar. –*C*), 136.0 (Ar. –*C*), 136.9 (Ar. –*C*), 139.0 (Ar. –*C*), 145.9 (Ar. –*C*). IR (cm^{-1}): 3431 (–N*H*–CH_2–), 3273 (–N*H*), 3064, 3001, 2972, 2919, 2866, 1606, 1584, 1520, 1506, 1470, 1448, 1395, 1361 (–SO_2), 1326, 1285, 1272, 1248, 1231, 1207, 1179, 1157 (–SO_2), 1093, 1070, 1048, 1027, 1000, 980, 932, 925, 906, 873, 852, 827, 813, 784, 757, 739, 729, 712, 686, 638, 597, 565, 553, 536, 489, 462. *Anal.* Calc. for: C: 68.82, H: 6.05, N: 7.64, O: 8.73, S: 8.75. Found: C: 68.90, H: 6.12, N: 7.60, S: 8.66%.

(**5**)-*N*-*[2-(benzylamino)-2,4,6-tri-methyl-phenyl]benzenesulfonamide*

Color: white. Yield: 86%. Mp: 152–153 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 2.32 (s, 3H, –(CH_3)$_p$), 2.33 (s, 6H, –(CH_3)$_o$), 4.15 (s, 2H, –C*H*$_2$–), 6.03–7.75 (13H, –N*H*–, *H*$_{1-4}$, –*H*$_{a-c}$, and –*H*$_y$). ^{13}C NMR ($CDCl_3$, ppm): 19.4 (–(CH_3)$_o$), 21.0 (–(CH_3)$_p$), 42.2 (–CH_2–), 111.9 (Ar. –*C*), 116.6 (Ar. –*C*), 120.3 (Ar. –*C*), 127.5 (Ar. –*C*), 128.5 (Ar. –*C*), 128.9 (Ar. –*C*), 129.1 (Ar. –*C*), 129.4 (Ar. –*C*), 131.4 (Ar. –*C*), 133.0 (Ar. –*C*), 137.3 (Ar. –*C*), 137.5 (Ar. –*C*), 139.0 (Ar. –*C*), 145.9 (Ar. –*C*). IR (cm^{-1}): 3413 (–N*H*–CH_2–), 3307 (–N*H*), 3073, 2964, 2923, 2872, 1601, 1584, 1509, 1475, 1447, 1377 (–SO_2), 1333, 1320, 1310, 1290, 1274, 1250, 1221, 1208, 1181, 1162 (–SO_2), 1121, 1089, 1073, 1063, 1048, 1022, 996, 933, 888, 854, 845, 826, 753, 728, 717, 691, 672, 632, 596, 570, 543, 500, 471. *Anal.* Calc. for: C: 69.44, H: 6,36, N: 7.36, O: 8.41, S: 8.43. Found: C: 69.54, H: 6,42, N:7.25, S:8.33%.



R= -C_6H_5 :(1) -*p*-methoxy-Ph :(2) -*p*-methyl-Ph: (3) -$C_6H_3Me_2$-2,4: (4) -$C_6H_2Me_3$-2,4,6: (5) -*p*-chloro-Ph: (6)

Fig. 1. Synthesis of the ligands together with NMR numbering scheme.

(**6**)-*N-[2-(benzylamino)-4-chloro-phenyl]benzenesulfonamide*

Color: light pink. Yield: 85%. Mp: 151–152 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 4.29 (s, 2H, –CH_2–), 6.28 (br. –NH–), 6.45–7.31 (9H, –H_{1-4}, –H_{x-z}), 7.47 (t, 2H, J = 8 Hz, –H_b), 7.60 (t, 2H, J = 8 Hz, –H_c), 7.78 (d, 2H, J = 8 Hz, –H_a). ^{13}C NMR ($CDCl_3$, ppm): 47.0 (–CH$_2$–), 112.2 (Ar. –C), 116.8 (Ar. –C), 120.2 (Ar. –C), 127.7 (Ar. –C), 128.6 (Ar. –C), 128.7 (Ar. –C), 128.9 (Ar. –C), 129.0 (Ar. –C), 129.5 (Ar. –C), 132.8 (Ar. –C), 133.2 (Ar. –C), 137.5 (Ar. –C), 138.7 (Ar. –C), 145.7 (Ar. –C). IR (cm^{-1}): 3439 (–NH–CH$_2$–), 3209 (–NH), 3066, 3047, 3033, 2964, 2936, 2903, 2854, 1602, 1581, 1516, 1489, 1468, 1448, 1436, 1409, 1360 (–SO$_2$), 1317, 1290, 1281, 1253, 1206, 1180, 1148 (–SO$_2$), 1129, 1090, 1073, 1049, 1026, 1014, 1001, 993, 939, 921, 856, 832, 806, 756, 745, 731, 711, 684, 639, 596, 556, 533, 472, 456. *Anal.* Calc. for: C: 61.20, H: 4.60, N: 7.51, O: 8.58, S: 8.60. Found: C: 61.32, H: 4.50, N: 7.60, S: 8.48%.

2.3. General procedure for the synthesis of 7–12

A solution of **1–6** (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 reaction mixture was stirred for 12 h. 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 in MeOH and black-colored microcrystals were obtained (Fig. 2).

2.3.1. Data for the 7–12

(**7**)-*{[N-[2-(benzylamino)-phenyl]benzenesulfonamide]-(p-cymene)-di-chloro-ruthenium(II)}*

Color: dark brown. Yield: 82%. Mp: 132–133 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 1.27 (d, 6H, J = 8 Hz, –H_m), 2.17 (s, 3H, –H_k), 2.92 (m, 1H, –H_l), 3.49 (s, 2H, –CH_2–), 5.34 (d, 2H, J = 8 Hz, –H_t), 5.49 (d, 2H, J = 8 Hz, –H_q), 6.66–8.12 (16H, –NH– H_{1-4}, –H_{a-c}, and –H_{x-z}). ^{13}C NMR ($CDCl_3$, ppm): 19.0 (–CH$_3$), 22.1 (–CH(CH$_3$)$_2$), 30.6 (–CH(CH$_3$)$_2$), 65.7 (–CH$_2$–), 80.5 (Ar. –C), 81.4 (Ar. –C), 82.0 (Ar. –C), 96.4 (Ar. –C), 101.0 (Ar. –C), 113.2 (Ar. –C), 113.8 (Ar. –C), 114.1 (Ar. –C), 114.3 (Ar. –C), 127.1 (Ar. –C), 127.4 (Ar. –C), 127.7 (Ar. –C), 128.0 (Ar. –C), 128.4 (Ar. –C), 128.9 (Ar. –C), 129.0 (Ar. –C), 129.1 (Ar. –C), 129.8 (Ar. –C), 134.2 (Ar. –C). IR (cm^{-1}): 3425 (–NH–CH$_2$–), 3215 (–NH), 3056, 2963, 2925, 2903, 2873, 1645, 1599, 1585, 1531, 1528, 1520, 1496, 1489, 1471, 1464, 1447, 1409, 1368, 1379, 1362 (–SO$_2$), 1325, 1310, 1294, 1261, 1260, 1201, 1157 (–SO$_2$), 1114, 1085, 1058, 1033, 1005, 914, 877, 804, 752, 732, 720, 689, 671, 646, 627, 610, 583, 559, 526, 507, 497, 493, 484, 459. *Anal.* Calc. for: C: 54.03, H: 5.00, Cl: 11.00, N: 4.35, O: 4.96, Ru: 15.68, S: 4.97. Found: C: 54.15, H: 4.94, N: 4.23, S: 4.86%.

(**8**)-*{[N-[2-(benzylamino)-4-methoxy-phenyl]benzenesulfonamide]-(p-cymene)-di-chloro-ruthenium(II)}*

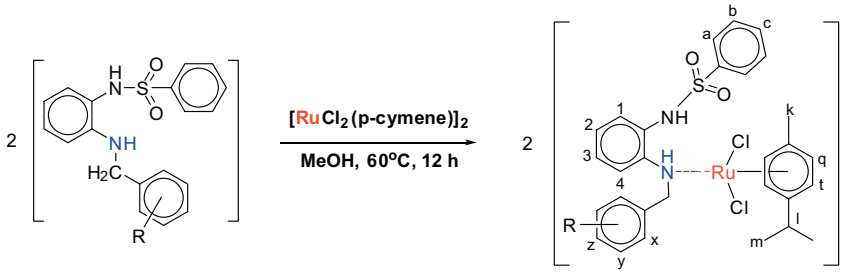
Color: dark brown. Yield: 78%. Mp: 122–123 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 1.28 (d, 6H, J = 8 Hz, –H_m), 2.16 (s, 3H, –H_k), 2.92 (m, 1H, –H_l), 3.81 (s, 3H, –OCH_3), 3.75 (s, 2H, –CH_2–), 5.35 (d, 2H, J = 8 Hz, –H_t), 5.48 (d, 2H, J = 8 Hz, –H_q), 6.61–7.99 (15H, –NH– H_{1-4}, –H_{a-c}, and –H_{x-y}). ^{13}C NMR ($CDCl_3$, ppm): 18.9 (–CH$_3$), 22.2 (–CH(CH$_3$)$_2$), 30.7 (–CH(CH$_3$)$_2$), 55.2 (–OCH$_3$), 65.9 (–CH$_2$–), 80.6 (Ar. –C), 81.3 (Ar. –C), 82.1 (Ar. –C), 96.8 (Ar. –C), 101.3 (Ar. –C), 113.9 (Ar. –C), 114.0 (Ar. –C), 114.1 (Ar. –C), 114.3 (Ar. –C), 127.3 (Ar. –C), 127.4 (Ar. –C), 127.6 (Ar. –C), 128.4 (Ar. –C), 128.6 (Ar. –C), 128.9 (Ar. –C), 129.1 (Ar. –C), 129.2 (Ar. –C), 129.3 (Ar. –C), 133.2 (Ar. –C). IR (cm^{-1}): 3434 (–NH–CH$_2$–), 3242 (–NH), 3055, 2961, 2906, 2867, 2836, 1608, 1584, 1511, 1488, 1471, 1464, 1445, 1386, 1323 (–SO$_2$), 1305, 1290, 1247, 1155 (–SO$_2$), 1115, 1087, 1058, 1026, 913, 825, 805, 751, 730, 719, 687, 666, 625, 582, 555, 517, 499, 491, 455. *Anal.* Calc. for: C: 53.25, H: 5.36, Cl: 10.48, N: 4.14, O: 7.09, Ru: 14.94, S: 4.74. Found: C: 53.87, H: 5.30, N: 4.33, S: 4.96%.

(**9**)-*{[N-[2-(benzylamino)-4-methyl-phenyl]benzenesulfonamide]-(p-cymene)-di-chloro-ruthenium(II)}*

Color: black. yield: 80%. Mp: 166–168 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 1.29 (d, 6H, J = 8 Hz, –H_m), 2.16 (s, 3H, –H_k), 2.29 (s, 3H, –CH$_3$), 2.93 (m, 1H, –H_l), 3.50 (s, 2H, –CH_2–), 5.36 (d, 2H, J = 8 Hz, –H_t), 5.49 (d, 2H, J = 8 Hz, –H_q), 6.94–8.06 (15H, –NH–, H_{1-4}, –H_{a-c}, and –$H_{x,y}$). ^{13}C NMR ($CDCl_3$, ppm): 18.9 (–CH$_3$), 21.3 (–CH$_3$)$_p$, 22.2 (–CH(CH$_3$)$_2$), 25.4 (–CH(CH$_3$)$_2$), 60.7 (–CH$_2$–), 80.6 (Ar. –C), 81.3 (Ar. –C), 96.8 (Ar. –C), 101.3 (Ar. –C), 116.9 (Ar. –C), 127.3 (Ar. –C), 127.6 (Ar. –C), 128.5 (Ar. –C), 129.0 (Ar. –C), 129.2 (Ar. –C), 129.3 (Ar. –C), 129.7 (Ar. –C), 129.9 (Ar. –C), 131.0 (Ar. –C), 131.3 (Ar. –C), 133.3 (Ar. –C). IR (cm^{-1}): 3413 (–NH–CH$_2$–), 3306 (–NH), 3056, 2965, 2923, 2873, 1645, 1602, 1515, 1499, 1489, 1472, 1447, 1388, 1378, 1362 (–SO$_2$), 1325, 1310, 1292, 1158 (–SO$_2$), 1087, 1057, 1035, 1005, 914, 878, 805, 754, 730, 689, 669, 626, 583, 560, 498, 482, 458. *Anal.* Calc. for: C: 54.54, H: 5.49, Cl: 10.73, N: 4.24, O: 4.84, Ru: 15.30, S: 4.85. Found: C: 54.42, H: 5.66, N: 4.34, S: 4.92%.

(**10**)-*{[N-[2-(benzylamino)-2,4-di-methyl-phenyl]benzenesulfonamide]-(p-cymene)-di-chloro-ruthenium(II)}*

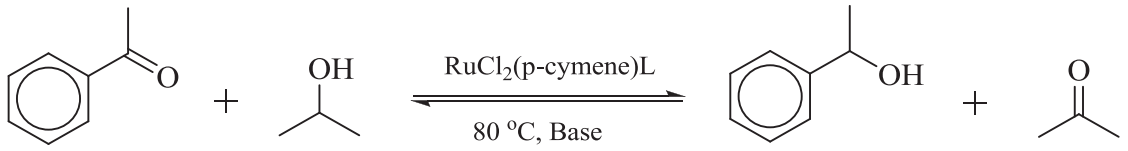
Color: black. Yield: 81%. Mp: 151–152 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 1.29 (d, 6H, J = 8 Hz, –H_m), 2.16 (s, 3H, –H_k), 2.40 (s, 3H, –(CH$_3$)$_o$), 2.64 (s, 3H, –(CH$_3$)$_p$), 2.91 (m, 1H, –H_l), 3.52 (s, 2H, –CH_2–), 5.36 (d, 2H, J = 8 Hz, –H_t), 5.49 (d, 2H, J = 8 Hz, –H_q), 6.63–7.80 (14H, –NH–, H_{1-4}, –H_{a-c}, and –H_{x-y}). ^{13}C NMR ($CDCl_3$, ppm): 18.9 (–CH$_3$), 19.5 (–(CH$_3$)$_o$), 21.1 (–(CH$_3$)$_p$), 22.2 (–CH(CH$_3$)$_2$), 30.6 (–CH(CH$_3$)$_2$), 47.1 (–CH$_2$–), 80.6 (Ar. –C), 81.4 (Ar. –C), 96.8 (Ar. –C), 101.3 (Ar. –C), 113.5 (Ar. –C), 118.6 (Ar. –C), 121.1 (Ar. –C), 126.8 (Ar. –C), 127.9 (Ar. –C), 128.0 (Ar. –C), 128.7 (Ar. –C), 129.1 (Ar. –C), 129.4 (Ar. –C), 132.6 (Ar. –C), 133.1 (Ar. –C), 133.3 (Ar. –C), 136.0 (Ar. –C), 136.8 (Ar. –C), 137.1 (Ar. –C), 140.6 (Ar. –C). IR (cm^{-1}): 3420 (–NH–CH$_2$–),



R= -C$_6$H$_5$:(7) -*p*-methoxy-Ph: (8) -*p*-methyl-Ph: (9) -C$_6$H$_3$Me$_2$-2,4: (10) -C$_6$H$_2$Me$_3$-2,4,6: (11) -*p*-chloro-Ph: (12)

Fig. 2. Synthesis of the complexes together with NMR numbering scheme.

Table 1
Catalytic activity for transfer hydrogenation of acetophenone catalyzed by Ru(II) complexes with different base.



Entry	Ru(II) complex	Base	Yield (%)[c]	TON[d]	TOF[e] (h^{-1})
1	7	NaOH	58[a], 72[b]	58[a], 72[b]	58[a], 36[b]
2	8		72[a], 80[b]	72[a], 80[b]	72[a], 40[b]
3	9		62[a], 75[b]	62[a], 75[b]	62[a], 38[b]
4	10		69[a], 78[b]	69[a], 78[b]	69[a], 39[b]
5	11		70[a], 77[b]	70[a], 77[b]	70[a], 39[b]
6	12		73[a], 82[b]	73[a], 82[b]	73[a], 41[b]
7	7	Et_3N	<5[b]	n.c.[b]	n.c.[b]
8	8		<5[b]	n.c.[b]	n.c.[b]
9	9		<5[b]	n.c.[b]	n.c.[b]
10	10		<5[b]	n.c.[b]	n.c.[b]
11	11		<5[b]	n.c.[b]	n.c.[b]
12	12		<5[b]	n.c.[b]	n.c.[b]
13	7	$KOBu^t$	42[a], 58[b]	42[a], 58[b]	42[a], 29[b]
14	8		60[a], 72[b]	60[a], 72[b]	60[a], 36[b]
15	9		54[a], 68[b]	54[a], 68[b]	54[a], 34[b]
16	10		48[a], 62[b]	48[a], 62[b]	48[a], 31[b]
17	11		55[a], 70[b]	55[a], 70[b]	55[a], 35[b]
18	12		60[a], 76[b]	60[a], 76[b]	60[a], 38[b]
19	Absence of catalyst	KOH (10 mmol)	11[a], 16[b]	11[a], 16[b]	11[a], 8[b]
20	12	Absence of base	<3[b]	n.c.[b]	n.c.[b]
21	12	KOH (1 mmol)	40[a]	40[a]	40[a]
23	12	KOH (0.1 mmol)	18[a]	18[a]	18[a]
24	12	KOH	21[a,f]	21[a]	21[a]
25	12	KOH	49[a,g]	49[a]	49[a]

Reaction conditions: 1.0 mmol of acetophenone, 10.0 mmol of Base, 0.01 mmol Ru(II) complexes, 2-propanol (20 mL); all reactions were monitored by TLC and GC; temperature 80 °C.
[a] 60 min.
[b] 120 min.
[c] GC yields, yields are based on phenylethanol.
[d] TON = moles of product/moles of the catalyst.
[e] TOF = moles of product/(moles of the catalyst) × (hour), n.c.: not calculated.
[f] T = ambient temperature °C.
[g] T = 50 °C.

3307 (–N*H*), 3056, 2968, 2920, 2902, 1644, 1596, 1500, 1472, 1464, 1446, 1406, 1387, 1379, 1361 ($–SO_2$), 1326, 1310, 1291, 1242, 1201, 1157 ($–SO_2$), 1086, 1056, 1037, 1000, 916, 878, 805, 753, 729, 688, 670, 626, 584, 558, 517, 480, 473, 463, 457. *Anal.* Calc. for: C: 55.19, H: 5.68, Cl: 10.51, N: 4.15, O: 4.74, Ru: 14.98, S: 4.75. Found: C: 55.25, H: 5.72, N: 4.22, S: 4.63%.

(**11**)-*{[N-[2-(benzylamino)-2,4,6-tri-methyl-phenyl]benzenesulfonamide]-(p-cymene)-di-chloro-ruthenium(II)}*

Color: light brown. Yield: 88%. Mp: 182–183 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 1.28 (d, 6H, J = 8 Hz, $–H_m$), 2.16 (s, 3H, $–H_k$), 2.26 (s, 6H, $–(CH_3)_o$), 2.29 (s, 3H, $–(CH_3)_p$), 2.92 (m, 1H, $–H_l$), 4.10 (s, 2H, $–CH_2–$), 5.35 (d, 2H, J = 8 Hz, $–H_t$), 5.48 (d, 2H, J = 8 Hz, $–H_q$), 6.63–7.80 (13H, –N*H*–, $H_{1–4}$, $–H_{a–c}$, and $–H_y$). ^{13}C NMR ($CDCl_3$, ppm): 18.9 ($–CH_3$), 19.6 ($–(CH_3)_o$), 21.0 ($–(CH_3)_p$), 22.2 ($–CH(CH_3)_2$), 30.7 ($–CH(CH_3)_2$), 42.4 ($–CH_2–$), 80.5 (Ar. –*C*), 81.3 (Ar. –*C*), 96.8 (Ar. –*C*), 101.2 (Ar. –*C*), 109.4 (Ar. –*C*), 111.9 (Ar. –*C*), 114.2 (Ar. –*C*), 116.6 (Ar. –*C*), 120.3 (Ar. –*C*), 127.3 (Ar. –*C*), 127.6 (Ar. –*C*), 128.9 (Ar. –*C*), 129.2 (Ar. –*C*), 129.8 (Ar. –*C*), 131.4 (Ar. –*C*), 133.0 (Ar. –*C*), 137.3 (Ar. –*C*), 137.5 (Ar. –*C*), 139.0 (Ar. –*C*), 145.9 (Ar. –*C*). IR (cm^{-1}): 3413 (–N*H*–CH_2–), 3307 (–N*H*), 3032, 2966, 2921, 2902, 2873, 1601, 1584, 1510, 1473, 1448, 1409, 1378, 1333 ($–SO_2$), 1321, 1310, 1290, 1275, 1250, 1222, 1208, 1181, 1163, 1121 ($–SO_2$), 1090, 1073, 1057, 1049, 1037, 1006, 997, 933, 889, 863, 854, 845, 827, 805, 759, 754, 729, 717, 692, 633, 598, 571, 544, 500, 478, 472. *Anal.* Calc. for: C: 55.81, H: 5.85, Cl: 10.30, N: 4.07, O: 4.65, Ru: 14.68, S: 4.66. Found: C: 55.91, H: 5.77, N: 4.01, S: 4.53%.

(**12**)-*{[N-[2-(benzylamino)-4-chloro-phenyl]benzenesulfonamide]-(p-cymene)-di-chloro-ruthenium(II)}*

Color: dark brown. Yield: 85%. Mp: 160–161 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 1.29 (d, 6H, J = 8 Hz, $–H_m$), 2.16 (s, 3H, $–H_k$), 2.90 (m, 1H, $–H_l$), 4.21 (s, 2H, $–CH_2–$), 5.36 (d, 2H, J = 8 Hz, $–H_t$), 5.49 (d, 2H, J = 8 Hz, $–H_q$), 6.62–7.88 (15H, –N*H*– $H_{1–4}$, $–H_{a–c}$, and $–H_{x–y}$). ^{13}C NMR ($CDCl_3$, ppm): 19.2 ($–CH_3$), 22.3 ($–CH(CH_3)_2$), 30.7 ($–CH(CH_3)_2$), 66.2 ($–CH_2–$), 80.7 (Ar. –*C*), 81.6 (Ar. –*C*), 82.6 (Ar. –*C*), 96.7 (Ar. –*C*), 101.4 (Ar. –*C*), 113.5 (Ar. –*C*), 114.0 (Ar. –*C*), 114.4 (Ar. –*C*), 114.5 (Ar. –*C*), 127.4 (Ar. –*C*), 127.5 (Ar. –*C*), 127.9 (Ar. –*C*), 128.0 (Ar. –*C*), 128.8 (Ar. –*C*), 129.2 (Ar. –*C*), 129.4 (Ar. –*C*), 129.9 (Ar. –*C*), 130.0 (Ar. –*C*), 135.1 (Ar. –*C*). IR (cm^{-1}): 3460 (–N*H*–CH_2–), 3278 (–N*H*), 3059, 2955, 2920, 2900, 2888, 1628, 1600, 1578, 1520, 1518, 1505, 1490, 1486, 1465, 1462, 1438, 1400, 1372, 1366, 1355 ($–SO_2$), 1313, 1300, 1290, 1269, 1255, 1200, 1166 ($–SO_2$), 1117, 1092, 1052, 1030, 1003, 916, 872, 801, 742, 722, 710, 682, 661, 641, 621, 613, 588, 565, 523, 517, 487, 482, 480, 455. *Anal.* Calc. for: C: 51.29, H: 4.60, Cl: 15.66, N: 4.13, O: 4.09, Ru: 14.88, S: 4.72. Found: C: 51.35, H: 4.52, N: 4.23, S: 4.66%.

2.4. General procedure for the transfer hydrogenation reaction

In a typical experiment, 0.01 mmol of [(*p*-cymene)$RuLCl_2$], 1 mmol of acetophenone and 10 mmol of KOH were refluxed at 80 °C in 2-propanol (20 ml) as a hydrogen source. After the mixture was cooled to room temperature, one-fourth of the 2-propanol were removed under reduced pressure (not dried). The residues

were 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. The reactions were conducted at a (S/C/base) molar ratio of 1:0.01:10.

3. Results and discussion

The synthesis and reaction routes of the Ru(II) complexes are presented in Fig. 2. The synthesized compounds were characterized by ^{1}H NMR, ^{13}C NMR and IR spectroscopy techniques.

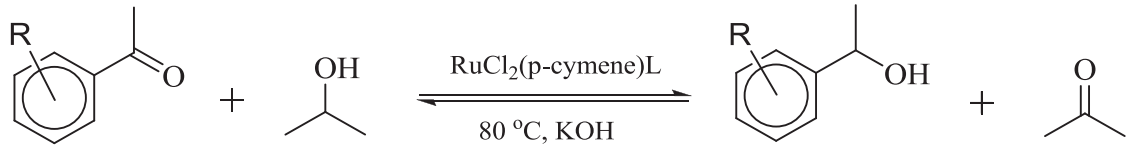
1–6 were obtained by the reaction of *N*-[2-(benzylamino)phenyl]benzenesulfonamide with solid sodium borohydride in methyl alcohol. Then, the novel ruthenium complexes (**7**–**12**) were synthesized by the reaction of **1**–**6** with $[RuCl_2(p\text{-}cymene)]_2$ in methyl alcohol. Moreover, [(*p-cymene*)$RuLCl_2$] (**7**–**12**) were used as catalysts for the TH of acetophenone derivatives.

3.1. NMR spectra

In the ^{1}H NMR spectra for *N*-[2-(benzylamino)-phenyl]benzenesulfonamide ligands (**1**–**6**), the $-H_a$, $-H_b$ and $-H_c$ protons were observed, respectively, as doublets, triplets and triplets in a 2:2:1 ratio at around δ 7.46–7.80 ppm. In the ^{1}H NMR spectra for the reduced imine ligands (**1**–**6**), –NH–CH_2– proton peaks appeared as singlets at δ 4.30, 3.83, 4.25, 4.19, 4.15 and 4.29 ppm, respectively. In (**z**) position, $-p-OCH_3$ and $-p-CH_3$ protons were observed as singlets at δ 3.83 ppm for (**2**) and at δ 2.35 ppm for (**3**); $-(CH_3)_o$ and $-(CH_3)_p$ protons were also observed as singlets at δ 2.34 and 2.32 ppm for (**4**) and at δ 2.33 and 2.32 ppm for (**5**), respectively. In the ^{13}C NMR spectra for the reduced imine ligands (**1**–**6**), the –NH–CH_2– carbons were observed at δ 48.1, 47.26, 48.22, 45.7, 42.2 and 47.0 ppm, respectively. Similarly, in (**z**) position, $-p-OCH_3$ and $-p-CH_3$ carbons appeared at δ 55.2 ppm for (**2**), and at δ 21.1 ppm for (**3**); $-(CH_3)_o$ and $-(CH_3)_p$ carbons were observed at δ 21.0 and 18.9 ppm for (**4**) and at δ 21.0 and 19.4 ppm for (**5**), respectively.

In the ^{1}H NMR spectra of the Ru(II) complexes (**7**–**12**) bearing reduced imine ligands, the ^{1}H NMR signals shifted to lower fields for the –NH–CH_2– protons compared with **1**–**6** and were observed at around δ 3.49–4.21 ppm in **7**–**12**. In (**z**) position, $-p-OCH_3$ and $-p-CH_3$ protons were observed as singlets at δ 3.81 ppm for (**8**) and at δ 2.29 ppm for (**9**); $-(CH_3)_o$ and $-(CH_3)_p$ protons were also observed as singlets at δ 2.40 and 2.64 ppm for (**10**) and at δ 2.26 and 2.29 ppm for (**11**), respectively. Additionally, $-H_k$, $-H_q$, $-H_t$, $-H_l$ and $-H_m$ protons relating to *p*-cymene exhibited, respectively, at 2.17, 5.49, 5.34, 2.92, 1.27 ppm in **7**; at 2.16, 5.49, 5.35, 2.92, 1.28 ppm in **8**; at 2.16, 5.49, 5.36, 2.93, 1.29 ppm in **9**; at 2.16, 5.49, 5.36, 2.91, 1.29 ppm in **10**; at 2.16, 5.48, 5.35, 2.92,

Table 2
Catalytic activity for transfer hydrogenation of ketones catalyzed by Ru(II) complexes.



Entry	Ru(II) complex	Substrate	Yield (%)[d]	TON[e]	TOF[f] (h^{-1})
1	7		64[a], 90[b]	64[a], 90[b]	256[a], 180[b]
2	8		69[a], 90[b]	69[a], 90[b]	276[a], 180[b]
3	9		74[a], 92[b]	74[a], 92[b]	296[a], 184[b]
4	10		58[a], 90[b]	58[a], 90[b]	232[a], 180[b]
5	11		62[a], 87[b]	62[a], 87[b]	248[a], 174[b]
6	12		78[a], 98[b]	78[a], 98[b]	312[a], 196[b]
7	7		81[c]	81[c]	81[c]
8	8		80[c]	80[c]	80[c]
9	9		83[c]	83[c]	83[c]
10	10		78[c]	78[c]	78[c]
11	11		84[c]	84[c]	84[c]
12	12		88[c] (33[b])	88[c](33[b])	88[c] (66[b])
13	7		100[b]	100[b]	200[b]
14	8		100[b]	100[b]	200[b]
15	9		100[b]	100[b]	200[b]
16	10		100[b]	100[b]	200[b]
17	11		100[b]	100[b]	200[b]
18	12		100[b] (56[a])	100[b] (56[a])	200[b] (224[a])
19	12		46[b,g]	230 [b,g]	460[b,g]
20	12		42[b,h]	210 [b,h]	840[b,h]
21	7		85[c]	85[c]	85[c]
23	8		87[c]	87[c]	87[c]
24	9		91[c]	91[c]	91[c]
25	10		89[c]	89[c]	89[c]
26	11		90[c]	90[c]	90[c]
27	12		94[c] (38[b])	94[c] (38[b])	94[c] (76[b])

Reaction conditions: 1.0 mmol of substrate, 10.0 mmol of KOH, 0.01 mmol Ru(II) complexes, 2-propanol (20 mL); all reactions were monitored by TLC and GC; temperature 80 °C.

[a] 15 min.
[b] 30 min.
[c] 60 min.
[d] GC yields, yields are based on phenylethanol.
[e] TON = moles of product/moles of the catalyst.
[f] TOF = moles of product/(moles of the catalyst) × (hour).
[g] S/C = 500/1.
[h] S/C = 1000/1.

1.28 ppm in **11**; at 2.16, 5.49, 5.36, 2.90, 1.29 ppm in **12**. In the ^{13}C NMR spectra for Ru(II) complexes (**7**–**12**), the –NH–CH_2– carbons were observed at δ 65.7, 65.9, 60.7, 47.1, 42.4 and 66.2 ppm, respectively. Similarly, in (**z**) position, –*p*–OCH_3 and –*p*–CH_3 carbons appeared at δ 55.2 ppm for (**8**), and at δ 21.3 ppm for (**9**); –$(CH_3)_o$ and –$(CH_3)_p$ carbons were observed at δ 19.5 and 21.1 ppm for (**10**) and at δ 19.6 and 21.0 ppm for (**11**), respectively. The representative NMR spectrums are attached in Fig. S1 as supplementary material.

3.2. Catalytic studies

Catalytic studies with **7**–**12** were performed for the TH of acetophenone to give phenylethanol in the presence of base by 2-propanol as a hydrogen source (Table 1). 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 unfavorable equilibrium. As the starting point, the performances of the catalysts in the transfer hydrogenation were screened by using acetophenone as a model substrate.

In the transfer hydrogenation 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 transfer hydrogenation of ketones. Acetophenone was kept as a test substrate and allowed it to react in isopropanol with catalytic quantities of complexes **7**–**12** in the presence of different bases like KOH, NaOH, Et_3N and $KOBu^t$. It has been observed that NaOH and KOH have good conversion when compared to Et_3N and $KOBu^t$ in TH reactions. The stronger the base the higher the general conversion rankings, KOH > NaOH > $KOBu^t$ > Et_3N. As in previous studies the best results were obtained with KOH [37,72]. Hence, it is decided that base KOH is the best compromise for optimum reaction rate in isopropanol and reaches 98% conversion for acetophenone within 30 min (Table 1). In the absence of a base no TH of the ketones was observed. Further, the effect of KOH was investigated in different concentration (10, 1, 0.1 mmol) (Table 1). Moreover, in the absence of catalyst TH of acetophenone with 10 mmol KOH was observed as only 16% conversion at 2 h.

A few of *p*-substituent acetophenone derivatives were transformed to the corresponding secondary alcohols. Typical results are shown in Table 2. Under these conditions *p*-methoxyacetophenone and *p*-chloroacetophenone react very cleanly and in good yields with 2-propanol (Table 2, entries 13–27). The presence of electron withdrawing (Cl) or electron donating (OCH_3) substituents on acetophenone has a significant effect on the reduction of ketones to their corresponding alcohols. The maximum conversion of 4- chloroacetophenone to corresponding alcohol was achieved over a period of 30 min. (Table 2, entries 13–20). The effect of catalyst concentration was also investigated (Table 2, entries 19, 20). Among the tested complexes, the complex **12** is highly efficient in the transfer hydrogenation of ketone to secondary alcohol. All the experiments were carried out in an air atmosphere. This indicates that air is not involved in the TH process and arene ruthenium(II) complexes are air-stable.

4. Conclusion

In epitome, we have reported the preparation and characterization of aryl sulfonamide ligands (**1**–**6**), neutral sulfonamide–Ru(II) complexes (**7**–**12**) and their catalytic activities for the TH of acetophenone derivatives by using 2-propanol in the presence of base. The procedure is simple and efficient towards various aryl ketones. Although all of the complexes are active catalysts for the TH of ketones, conversion was not screened with an organic base such as Et_3N. Ru(II) arene complexes was observed more efficient catalysts for electron-withdrawing substituent –Cl on the *para* position of aryl ring of the ketones. Furthermore, the presence of electron-withdrawing group on the sulfonamide-ring has a beneficial effect. Consequently, complex **12** was observed the most active complex (turnover frequency value: **840** h^{-1} molar ratio S/C: 1000/1). When examined to TH of Ru(II) arene complexes in the literature, it is seen that catalysts used in this study have been an passable efficiency in the TH [74–79].

Acknowledgment

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.03.004.

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