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# Ruthenium carbonyl compounds containing polypyridine ligands as catalysts in the reaction of N-benzylideneaniline hydrogenation

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ABSTRACT

The synthesis and characterization of ruthenium complexes containing polypyridine ligands: $Ru(dppz)(PPh_3)_2Cl_2$, $Ru(bpy)(PPh_3)_2Cl_2$, $Ru(phen)(PPh_3)_2Cl_2$, $Ru(dppz\text{-}Cl)(PPh_3)_2Cl_2$, $Ru(phen)(CO)_2Cl_2$, $Ru(bpy)(CO)_2Cl_2$ and $Ru(dppz)(CO)_2Cl_2$ (where dppz: dipyrido[3,2-*a*:2′,3′-*c*]phenazine, dppz-Cl: 10-chlororodypirido[3,2-*a*:2′,3′-*c*] phenazine, phen: 1,10-phenanthroline and bipy: 2,2′-bipyridine) are reported. The ruthenium complexes show high activity as catalysts in the hydrogenation reaction of N-benzylideneaniline and the hydrogen transfer reaction. The products of the catalysis were obtained with conversions between 21 and 91% after 2 h of reaction. The $Ru(phen)(CO)_2Cl_2$ complex was the catalyst that showed the highest conversion (91%) for the hydrogenation of N-benzylideneaniline. The complexes $Ru(dppz)(PPh_3)_2Cl_2$, $Ru(bpy)(PPh_3)_2Cl_2$ and $Ru(dppz)(CO)_2Cl_2$ showed 99% conversion in the hydrogen transfer reaction.



**Introduction**: The hydrogen transfer reaction of polar functional groups has significantly contributed to the recent growth in the area of organic synthesis [1]. The reaction is recommended for its simplicity since no hydrogen gas is required. When propan-2-ol is used as the hydrogen donor, the only by-product formed is acetone, which is easily removed by distillation during workup. While the transfer hydrogenation reaction of ketones [1–3] has been widely explored during the last two decades, the corresponding reaction of imines [1,4,5] has been less studied (Scheme 1). The hydrogenation of imines using $[RuCl_2(PPh_3)_3]$, propan-2-ol, and $K_2CO_3$ as base was carried out nearly a decade ago [4,5]. Noyori et al. reported the first asymmetric transfer hydrogenation of imines by formic acid using a chiral ruthenium catalyst with excellent yields and enantioselectivities. More recently, Baker and Mao reported transfer hydrogenation of imines by formic acid using chiral Noyori ligands on a Rhodium catalyst [5]. No asymmetric transfer hydrogenation of imines by propan-2-ol has been reported so far. Some additional recent contributions of transfer hydrogenation of imines include Ru(II) [6,7], Rh(III) [8,9], Ir(III) [10] and Ni(0) [11] catalysts. The proposed mechanism for transfer hydrogenation of ketones and imines with ruthenium complex involves a step where the hydride and the proton are transferred from the catalyst to the substrate in a concerted reaction without coordination of the substrate.

We report the synthesis and characterization of ruthenium complexes containing polypyridine ligands: $Ru(dppz)(PPh_3)_2Cl_2$, $Ru(bpy)(PPh_3)_2Cl_2$, $Ru(phen)(PPh_3)_2Cl_2$ $Ru(dppz\text{-}Cl)(PPh_3)_2Cl_2$, $Ru(phen)(CO)_2Cl_2$, $Ru(dppz)(CO)_2Cl_2$ and $Ru(bpy)(CO)_2Cl_2$ (where dppz: dipyrido[3,2-*a*:2′,3′-*c*]phenazine, dppz-Cl:10-chlororodypirido [3,2-*a*:2′,3′-*c*]phenazine, phen: 1,10-phenanthroline and bipy: 2,2′-bipyridine). The complexes were used in homogeneous catalytic processes to transfer hydrogen from 2-propanol towards N-benzylideneaniline (Scheme 1). The compounds $Ru(bpy)(PPh_3)_2Cl_2$, $Ru(dppz)(PPh_3)_2Cl_2$ and $Ru(phen)(PPh_3)_2Cl_2$ were successfully synthesized using the procedure for $Ru(dppz\text{-}Cl)(PPh_3)_2Cl_2$. The products of the catalytic reaction were obtained in high yields with conversions in the range of 21–91% after 2 h of reaction with N-benzylideneaniline. The best conversion was obtained using the $Ru(phen)(CO)_2Cl_2$ complex as catalyst (91%).

**Experimental**: $^1$H-NMR and $^{31}$P-NMR spectra were recorded on a 350 MHz Bruker spectrometer. The precursor, $Ru(PPh_3)_3Cl_2$, was synthesized by a procedure previously described [12] without modifications. The procedure of synthesis of the complexes $Ru(bpy)(CO)_2Cl_2$, $Ru(phen)(CO)_2Cl_2$ and $Ru(dppz)(CO)_2Cl_2$ have been published previously [13]. The complexes *trans*-$PPh_3$-$[Ru(dppz)(PPh_3)_2Cl_2$ (**1**) and *trans*-$PPh_3$-$[Ru(dppz\text{-}Cl)(PPh_3)_2Cl_2$ (**2**) *trans*-$PPh_3$-$[Ru(bpy)(PPh_3)_2Cl_2$

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**Scheme 1.** Hydrogenation of N-benzylideneaniline by a new ruthenium (II) complex derivated from polypyridine ligands.

(**3**) [14] *trans*-$PPh_3$-[Ru(phen)$(PPh_3)_2Cl_2$ [15] (**4**) were synthesized from $Ru(PPh_3)_3Cl_2$.[1] The complex $Ru(bpy)_2Cl_2$ and $Ru(phen)_2Cl_2$ were synthesized using the procedure reported in the literature[16]. The N-benzylideneaniline hydrogenation was conducted using iso-propanol in a basic medium with a ratio of substrate/catalyst = 400 and a ratio of KOH/Ru = 20. A similar procedure was used in the transfer hydrogenation reaction of acetophenone with a ratio substrate/catalyst = 1000/1. All experiments were analyzed by GC-chromatography[2] using a HP-5 column.

$RuCl_2(PPh_3)_3$ reacted with one equivalent of dppz, bpy and phen ligands, in dichloromethane at room temperature, with high yield. The paternal signals in $^1$H-NMR and $^{31}$P-NMR confirm the structure proposed for these compounds and for the complexes and they are in accordance with the elemental analysis and the IR spectrum. The complexes *trans*-$PPh_3$-[Ru(bpy)$(PPh_3)_2Cl_2$, *trans*-$PPh_3$-[Ru(phen)$(PPh_3)_2Cl_2$ *trans*-$PPh_3$-[Ru(dppz)$(PPh_3)_2Cl_2$ and *trans*-$PPh_3$-[Ru(dppz-Cl)$(PPh_3)_2Cl_2$ were obtained in high yield. The compounds were obtained in an octahedral coordination with the phosphine group appearing in a *trans*-configuration which was confirmed by $^{31}$P-NMR. The complexes Ru(bpy)$(CO)_2Cl_2$ and Ru(phen)$(CO)_2Cl_2$ and Ru(dppz)$(CO)_2Cl_2$ used in this work show the paternal signal similar to those reported previously by us [13]. The compounds were studied as catalysts in the transfer hydrogenation reaction of imine and ketone.

Table 1 shows the catalytic activity in the hydrogen transfer reaction of acetophenone catalyzed by compounds of ruthenium (II) with polypyridine ligands. The activities displayed by these compounds vary between 50 and 97 in 30 min of reaction (entries 1–7). When comparing the catalytic activity of these compounds with the precursors $Ru(PPh_3)_3Cl_2$ and $[Ru(CO)_2(Cl)_2]_n$ (entries 8–9) used for the synthesis of the complexes, it was observed that the catalytic activity increased significantly with the presence of a polypyridine ligand in the coordination sphere of the metal. The presence of the polypyridine ligand stabilizes the metal in catalytic conditions thus enabling the reaction that forms ruthenium hydride, which is the active species for this reaction. The compounds Ru(dppz)$(PPh_3)_2Cl_2$ and Ru(bpy)$(PPh_3)_2Cl_2$ and Ru(dppz)$(CO)_2Cl_2$ were the most active after 30 min of reaction. After 2 h of reactions, complexes 1, 4–7 have shown activities near 99%, however compound 3 shows 63%. This is the consequence of an increased electron density on the metal provided by the polypiridine ligand. On the other hand the compounds Ru(bpy)$_2Cl_2$ and Ru(phen)$_2Cl_2$ were not active catalysts in the hydrogen transfer of acetophenone maybe because the lower solubility of complexes or the steric effect did not allow the formation of the hydride–ruthenium complex.

**Table 1**
Catalytic activity in hydrogen transfer reaction of acetophenone.

| Run | Catalyst/time (minutes) | Conversion (%); (TOF $h^{-1}$) | | | |
|---|---|---|---|---|---|
| | | 30 | 60 | 90 | 120 |
| 1 | Ru(dppz)$(PPh_3)_2Cl_2$ (**1**) | 91; (1820) | 96; (960) | 98; (653) | 99; (495) |
| 2 | Ru(dppz-cl)$(PPh_3)_2Cl_2$ (**2**) | 56; (1120) | 67; (670) | 74; (493) | 78; (390) |
| 3 | Ru(phen)$(PPh_3)_2Cl_2$ (**3**) | 50; (1000) | 56; (560) | 59; (393) | 63; (315) |
| 4 | Ru(bpy)$(PPh_3)_2Cl_2$ (**4**) | 96; (1920) | 97; (970) | 99; (660) | 99; (495) |
| 5 | Ru(bpy)$(CO)_2Cl_2$ (**5**) | 64; (1280) | 90; (900) | 96; (640) | 97; (485) |
| 6 | Ru(phen)$(CO)_2Cl_2$ (**6**) | 74; (1480) | 93; (930) | 95; (633) | 98; (490) |
| 7 | Ru(dppz)$(CO)_2Cl_2$ (**7**) | 97; (1940) | 98; (980) | 99; (660) | 99; (495) |
| 8 | $Ru(PPh_3)_3Cl_2$ (**8**) | 2; (40) | 3; (30) | 3; (20) | 3; (15) |
| 9 | $[Ru(CO)_2Cl_2]_n$ (**9**) | 10 (200) | 14 (140) | 19; (126) | 24; (120) |
| 10 | Ru(phen)$_2Cl_2$ (**10**) | No active | | | |
| 11 | Ru(bpy)$_2Cl_2$ (**11**) | No active | | | |

Substrate/ruthenium = 1000; solvent = 2-propanol; base/ruthenium = 20.

Table 2 shows the catalytic activity of compounds of ruthenium (II) with polypyridine ligands in the hydrogenation of N-benzylideneaniline. Conversions range from 56 to 86% after 30 min of reaction (entries 1–6). When comparing the catalytic activity of the compounds Ru(dppz)$(PPh_3)_2Cl_2$ and Ru(dppz-Cl)$(PPh_3)_2Cl_2$ a reverse situation is observed compared to that seen in the hydrogen transfer reaction of acetophenone; in this case the activity of Ru(dppz-Cl)$(PPh_3)_2Cl_2$ is better than the one observed for Ru(dppz)$(PPh_3)_2Cl_2$. These results seem to be contradictory, as both catalytic processes of metal hydride formation are fundamental to the reaction and this intermediate is strongly favored by the presence of donor ligands. However, since the imine is basic it will react more rapidly with the more acidic metal, in this case with the complex containing the dppz-Cl ligand.

When the activities of complexes 1, 3 and 4 are compared, it can be seen that the activity showed by complex 1 is better than that of complex 3 and both have much better activity than complex 4. Even though the three different nitrogen ligands provide electronic effects, the differences observed in the activities cannot be rationalized on the basis of the small differences of the electronic effects. Probably the differences in the catalytic activities of these complexes are the consequence of the size of the nitrogen ligands. The higher the size of the ligands the less stable the formed complex becomes. Thus, the ligands dppz and phen should not form a very stable bond in

**Table 2**
Catalytic activity in the hydrogenation of N-benzylideneaniline.

| Run | Catalyst/time (minutes) | Conversion (%) (TOF $h^{-1}$) | | | |
|---|---|---|---|---|---|
| | | 30 | 60 | 90 | 120 |
| 1 | Ru(dppz)$(PPh_3)_2Cl_2$ (**1**) | 60; (480) | 72; (288) | 76; (202) | 83; (166) |
| 2 | Ru(dppz-cl)$(PPh_3)_2Cl_2$ (**2**) | 75; (600) | 83; (332) | 85; (226) | 88; (176) |
| 3 | Ru(phen)$(PPh_3)_2Cl_2$ (**3**) | 56; (448) | 60; (240) | 64; (171) | 69; (138) |
| 4 | Ru(bpy)$(PPh_3)_2Cl_2$ (**4**) | – | – | – | <5[a] |
| 5 | Ru(bpy)$(CO)_2Cl_2$ (**5**) | 65; (520) | 77; (308) | 83; (221) | 88; (176) |
| 6 | Ru(phen)$(CO)_2Cl_2$ (**6**) | 86; (688) | 88; (352) | 90; (240) | 91; (182) |
| 7 | Ru(dppz)$(CO)_2Cl_2$ (**7**) | 3; (24) | 5; (20) | 12; (32) | 21; (42)[b] |
| 8 | $Ru(PPh_3)_3Cl_2$ (**8**) | 0 | 0 | 0 | 0 |
| 9 | $[Ru(CO)_2Cl_2]_n$ (**9**) | 0 | 0 | 0 | 0 |
| 10 | Ru(phen)$_2Cl_2$ (**10**) | 0 | 0 | 0 | <5 |
| 11 | Ru(bpy)$_2Cl_2$ (**11**) | 0 | 0 | 0 | <5 |

Substrate/ruthenium = 400; solvent = 2-propanol; base/ruthenium = 20;
[a] The conversion increase after 10 h to 82%.
[b] The conversion increase after 10 h to 78%.

[1] Synthesis of the complexes. *Trans*-$PPh_3$-[Ru(dppz)$(PPh_3)_2Cl_2$ (**1**). $Ru(PPh_3)_2Cl_2$ (0.1 g, 1.0 mmol) and dipyrido[3,2-*a*:2′,3′-*c*]phenazine (0.029 g, 1.11 mmol) dissolved in chloroform, (20 mL) were placed into a round bottom flask. The mixture was stirred for 30 min. The solution was precipitated with ethyl ether; the solid obtained was filtered and washed with hexane and ethyl ether. The product was recrystallized (chloroform/ethyl ether). $^1$H-NMR (δ (ppm) $CDCl_3$): 9.3 (s, 1H), 8.4 (dd, 6 Hz, 4H), 8.0 (dd, 6 Hz, 4H), 7.1–6.9 (m, $PPh_3$). Anal. Calc. (%): for $C_{54}H_{40}N_4Cl_2N_4P_2$-Ru: C, 66.26; H, 4.12; N, 5.72. Found (%) C, 66.33; H, 4.38; N, 4.98. Yield 65%. *Trans*-$PPh_3$-[Ru(dppz-Cl)$(PPh_3)_2Cl_2$ (**2**). This compound was prepared by the same procedure used for the synthesis of *trans*-$PPh_3$-[Ru(dppz)$(PPh_3)_2Cl_2$. $^1$H-NMR (δ (ppm) $CDCl_3$): 9.1 (s, 2H), 9.0 (d, 7.7 Hz, 2H), 8.4 (s, 1H), 8.3 (d, 9.1 Hz, 1H) 7.9 (d, 9.1 Hz, 1H) 7.4–7.0 (m, $PPh_3$). Anal. Calc. (%): for $C_{54}H_{39}Cl_3N_4P_2$Ru: C, 64.01; H, 3.88; N, 5.53. Found (%) C, 64.21; H, 3.83; N, 5.21. Yield 70%.

[2] Catalytic hydrogenation. The catalyst precursor (0.012 mmol) was dissolved in 2-propanol (8 mL), and the solution was refluxed. After 10 min, a distilled amine compound (10 mmol) was added. After 10 min, the transfer hydrogenation reaction was initiated by addition of sodium hydroxide (9.9 mg, 0.24 mmol) dissolved in 2-propanol (1 mL). The progress of the reaction was monitored by gas chromatography with periodic sampling every 10 min. Gas chromatographic analysis was carried out with a Perkin Elmer 8500P instrument equipped with FID, using a Carbowax 20 M column and nitrogen as carrier gas. GC-Mass spectra were carried in order to confirm the identity of products in a MAT 95 XP Thermo Electron.

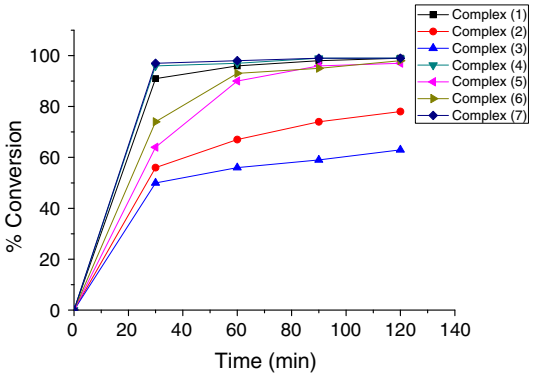


**Fig. 1.** Hydrogen transfer reaction using ruthenium complexes containing polypyridine ligands.

the product, Ru-benzylideneanilne, allowing the catalytic reaction to continue. Instead, the bond formed by the bipy ligand in the product, Ru-benzylidenaniline must be stable enough to stop and kill the catalytic process.

The catalytic activity in the hydrogenation of N-benzylideneaniline of polypyridine carbonyl compounds (see Table 2, entries 5–7). It is well known that the ligand CO stabilizes low oxidation states of the metal complexes of ruthenium. Considering this fact, we think that the addition of a CO ligand in the structure of the polypyridine complex could increase the catalytic potential of the system, by favoring the formation of the active species Ru–H. However the experimental data obtained for complexes of the type Ru(polypyridine)$(CO)_2Cl_2$ where the ligands polypyridine and CO coexist, do not show that the systems improve their catalytic activity with the incorporation of CO.

When the results obtained in this study for the complexes of the type Ru(L)$(PPh_3)_2Cl_2$ (with L = dppz, bpy, phen) are compared with the compounds Ru(L)$(CO)_2Cl_2$ (with L = bpy, phen, dppz) it becomes evident that for compounds Ru(bpy)$(L)_2Cl_2$ (L = CO or $PPh_3$) the activity is increased by replacing the phosphine ligand by a carbonyl ligand (entries 4 and 5). Similar behavior is obtained for the compound Ru(phen)$(CO)_2Cl_2$ (entries 3 and 6). An opposite behavior is observed with the compound Ru(dppz)$(CO)_2Cl_2$, (entries 1 and 7). Although the compound, Ru(dppz)$(CO)_2Cl_2$ exhibits low solubility in the reaction medium, its catalytic activity shows that our rationalization that the presence of carbonyl in the complex could help the formation of the species Ru–H increasing the catalytic activity is not conclusive and is currently under study.

Morris et al. [17] recently reported the hydrogenation of imines using molecular hydrogen. Molecular hydrogen is difficult to handle and requires special reactors working at high pressures. The same reaction can be performed using the hydrogen produced in the hydrogen transfer reaction, which allows working in glass reactors without extreme security measures. Using a hydrogen transfer reaction, Morris reported zero activity for the hydrogenation of N-benzylideneaniline catalyzed by ruthenium compounds. We report better activities than to those recently reported by us [18] and by Jia et al. [19], using the same substrate.

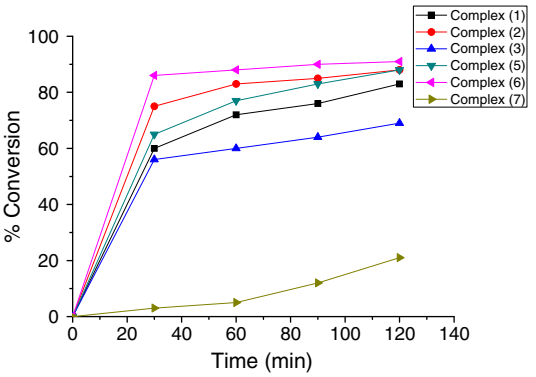


**Fig. 2.** Hydrogenation of N-benzylideneaniline using ruthenium complexes which contain polypyrdine ligands.

Fig. 1 shows the conversion and reaction time for the hydrogen transfer reaction. It is possible to observe that the rate for the reaction corresponding to the best systems studied decreased sharply after 30 min, but in all cases conversion exceeds 70%.

Graph 2 shows the conversion versus time for the hydrogenation reaction of N-benzylideneaniline using the hydrogen transfer reaction as a source of hydrogen. The reaction shows, that after 30 min, high conversions with high speed have been achieved. The activities of the catalysts show small differences, probably due to the different ability to coordinate the substrate, which could reduce the concentration of active metal in the reaction (Fig. 2).

**Conclusions**: Compounds of ruthenium (II) containing polypyridine and carbonyl ligands are active catalysts in the transfer hydrogenation reaction of N-benzylideneaniline by hydrogen transfer. The activities observed for short reaction times show high selectivity. Upon comparing the activity reported for different compounds it was observed that the compounds Ru(phen)$(CO)_2Cl_2$ and Ru(dppz-Cl)$(PPh_3)_2Cl_2$ and Ru(bpy)$(CO)_2Cl_2$ show better activity in the hydrogenation reaction of N-benzylideneaniline than those catalysts without nitrogen ligands. On the other hand complexes Ru(dppz)$(PPh_3)_2Cl_2$, Ru(bpy)$(PPh_3)_2Cl_2$ and Ru(dppz)$(CO)_2Cl_2$ showed 99% conversion in the hydrogen transfer reaction after 2 h reaction.

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