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Synthesis of ruthenium complexes with carbonyl and polypyridyl ligands derived from dipyrido[3,2-*a*:2′,3′-*c*]phenazine: application to the water gas shift reaction

P. Aguirre[1]*, R. López[2], D. Villagra[2], I. Azocar-Guzman[2], A. J. Pardey[3] and S. A. Moya[2]*

[1]Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile
[2]Departmento de Química de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile
[3]Escuela de Química, Facultad de Ciencias, Universidad Central, Caracas, Venezuela

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The preparation and spectroscopic properties of new dipyrido[3,2-*a*:2′,3′-*c*]phenazine ruthenium complexes are described. The complexes show high catalytic activity in the water gas shift reaction in a basic medium under mild conditions (P_{CO} = 0.9 atm at 100 °C). Copyright © 2002 John Wiley & Sons, Ltd.

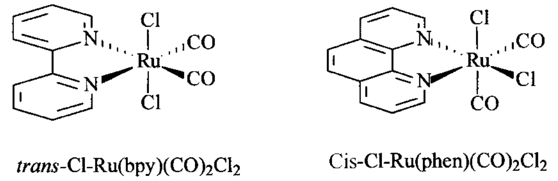
KEYWORDS: water gas shift reaction; ruthenium complexes; catalysts

INTRODUCTION

The synthesis and catalytic properties of polypyridine complexes of ruthenium have been extensively studied over a period of years, particularly those containing the ligand 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen). For example, bipyridyl and phenanthroline ruthenium carbonyl complexes (Fig. 1) have proved to be active catalysts in the water gas shift reaction[1] (WGSR) and in the electrochemical[2] and photochemical reduction of CO_2 to CO and formate.[3] In addition, several ruthenium complexes containing sterically hindered bpy or phen ligands have been used in other process such as the oxidation of organic substrates[4] and the hydrogenation of ketones and olefins.[5]

An efficient catalyst for the WGSR was obtained from $[Ir(dmp\text{-}S)(COD)]^+$ (dmp-S = the sulfonated derivative from 2,9-dimethyl-1,10-phenanthroline; COD = 1,5-cyclooctadiene) with a turnover frequency of 102 h^{-1} at 100 °C and 1 atm of CO) was reported.[6,7] Also, several rhodium complexes[8] have been reported to act as catalysts for the WGSR under varied conditions with observed turnover frequencies in the 7–75 h^{-1} range.

The ligand dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz)[9] (Fig. 2) coordinated to a metal center could have interesting properties that might affect the catalytic properties of a metal complex, namely planar structure, rigidity, presence of delocalized π system, and there is the possibility to modulate its electronic properties by introducing substituent groups, such as Cl and NO_2,[10] into its structure. In this work we report the synthesis of new carbonyl ruthenium complexes containing ligands derived from dppz and their behavior as catalysts in the WGSR.



trans-Cl-Ru(bpy)$(CO)_2Cl_2$ Cis-Cl-Ru(phen)$(CO)_2Cl_2$

Figure 1. Bipyridyl and phenanthroline ruthenium carbonyl complexes.

*Correspondence to: P. Aguirre, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile.
E-mail: paguirre@ciq.uchile.cl
**Correspondence to: S. A. Moya, Departmento de Químicas de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile.
E-mail: smoya@lauca.usach.cl
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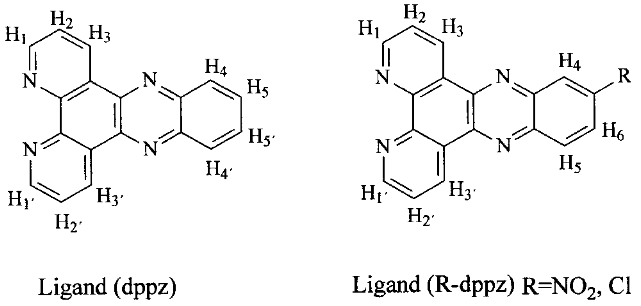


Ligand (dppz) Ligand (R-dppz) R=NO_2, Cl

Figure 2. The dipyrido[3,2-*a*:2′,3′-*c*]phenazine ligand.

EXPERIMENTAL

Materials

All chemicals were reagent grade and used as received unless otherwise noted. 1,10-Phenanthroline, $RuCl_3 \cdot xH_2O$, 1,2-phenylenediamine, 4-chloro-1,2-phenylenediamine, 4-nitro-1,2-phenylenediamine and chloroform-*d* were purchased from Aldrich and used as received. All solvents were carefully dried and distilled before use.

Synthesis

The Rdppz compounds (R = H, Cl, NO_2) were prepared according to literature procedures.[11,12] The ruthenium starting material, $[Ru(CO)_2Cl_2]_n$, was prepared by following previously reported procedures.[13,14] In a typical preparation a mixture of Rdppz and $[Ru(CO)_2Cl_2]_n$ (1:1 mole ratio) was suspended in ethanol–water (50 ml, 1:1). The mixture was stirred and refluxed for 2 h. The resulting solid was filtered, washed with ethanol and recrystallized from diethyl ether (Scheme 1).

11-Clorodipyrido[3,2-a:2′,3′-c]phenazine (Cldppz)

IR (KBr, cm^{-1}): 1605w, 1574m, 1517w, 1474s, 1403s, 1355s, 1205w, 1122s, 1109s, 1069s, 1052m, 1027m, 921m, 847s, 805s, 739s, and 616m. M.p. 240 °C (d). ^1H NMR (δ (ppm), $CDCl_3$): 9.51 (d, H_3,$H_{3'}$), 9.26 (d, H_1,$H_{1'}$), 8.27 (d, H_4), 8.24 (d, H_5), 7.83 (dd, H_6), 7.79 (m, H_2,$H_{2'}$). Anal. Found (%): C, 68.39; H, 2.79; N, 18.20. Calc. (%) for $C_{18}H_9ClN_4$: C, 68.25; H, 2.84; N, 17.69. Yield 65%.

11-Nitrodipyrido[3,2-a:2′,3′-c]phenazine (NO_2dppz)

IR (KBr, cm^{-1}): 1601m, 1523s, 1491m, 1455m, 1343s, 1298s, 1212m, 1091m, 1061s, 812s, and 746s. ^1H NMR (δ (ppm), $CDCl_3$): 9.62 (dd, H_3,$H_{3'}$), 9.32 (dd, H_1,$H_{1'}$), 9.27 (d, H_4), 8.68 (dd, H_6), 8.50 (d, H_5), 7.84 (m, H_2,$H_{2'}$). M.p. 328 °C (d). Anal. Found (%): C, 65.95; H, 2.70; N, 21.20. Calc. (%) for $C_{18}H_9N_5O_2$: C, 66.05; H, 2.75; N, 21.40. Yield 68%.

$[Ru(CO)_2(NO_2dppz)Cl_2]$

IR (KBr, cm^{-1}): 2063m, 1999m, 1618w, 1577m, 1551w, 1521s, 1480m, 1408m, 1343s, 1066m, 830m, 811m, and 738s. ^1H NMR (δ (ppm), $CDCl_3$): 9.91 (dd, H_3,$H_{3'}$), 9.64 (dd, H_1,$H_{1'}$), 9.40 (d, H_4), 8.83 (dd, H_6), 8.65 (d, H_5), 8.21 (m, H_2,$H_{2'}$). M.p 280 °C (d). Anal. Found (%): C, 43.31; H, 1.91; N, 11.96. Calc. (%) for $C_{20}H_9N_5Cl_2O_4Ru$: C, 43.24; H, 1.63; N, 12.61. Yield 84%.

$[Ru(CO)_2(Cldppz)Cl_2]$

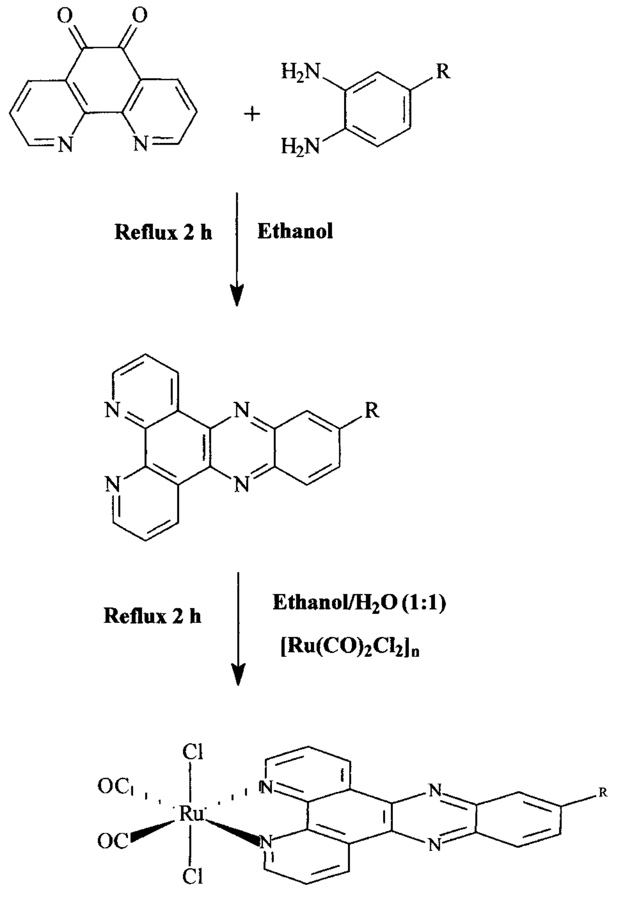
IR (KBr, cm^{-1}): 2065s, 2003s, 1598d, 1493m, 1463d, 1445d, 1412m, 1355m, 1082m, 1057m, 930d, 842d, 821d, and 730m. ^1H NMR (δ (ppm), $CDCl_3$): 9.87 (d, H_3,$H_{3''}$), 9.58 (dd, H_1,$H_{1'}$), 8.46 (d, H_4), 8.17 (d, H_5), 8.14 (m, H_2,$H_{2'}$), 8.02 (dd, H_6). M.p 330 °C. Anal. Found (%): C, 44.73; H, 1.71; N, 10.54. Calc. (%) for $C_{20}H_9N_4Cl_3O_2Ru$: C, 44.05; H, 1.65; N, 10.29. Yield 75%.

$[Ru(CO)_2(dppz)Cl_2]$

IR (KBr, cm^{-1}): 2066s, 2016s, 1602d, 1577m, 1551d, 1521f, 1480m, 1408m, 1343f, 1066m, 830m, 811m, and 738s. ^1H NMR (δ (ppm), $CDCl_3$): 9.90 (dd, H_3,$H_{3'}$), 9.58 (dd, H_1,$H_{1'}$), 8.44 (m, H_4,$H_{4'}$), 8.14 (m, H_5,$H_{5'}$), 8.04 (m, H_2,$H_{2'}$). M.p >400 °C. Anal. Found (%): C, 47.09; H, 2.44; N, 10.79. Calc. (%) for $C_{20}H_{10}Cl_2N_4O_2Ru$: C, 47.07; H, 1.96; N, 10.97. Yield 70%.

Measurements

IR spectra as KBr pellet were recorded on an FT-IFS 66v Fourier spectrophotometer. ^1H NMR spectra with chemical



Scheme 1.

shifts reported relative to tetramethylsilane were recorded on a Bruker DPX-300 MHZ spectrometer.

WGSR experiments

The homogeneous catalytic runs were carried out in 2-ethoxyethanol and in basic medium (KOH). Also, the catalytic runs were conducted in all-glass reactor vessels consisting of a 100 ml round-bottomed flask connected by an 'O' ring sealed joint and a two-way Rotoflow Teflon stopcock attached to the vacuum line.[15] In a typical catalytic experiment, an amount of the ruthenium complex (0.5 mM) dissolved in 5 ml of 2-ethoxyethanol, 0.54 ml of water (6 M) and KOH (0.6 M) was added to the glass reactor vessel containing a Teflon-coated stirring bar. The reaction mixture was degassed by three freeze–pump cycles. The reaction vessel was filled with CO at a given pressure such that the internal partial pressure of CO reached the desired value at the temperature of the experiment (typically, 0.9 atm CO at 100 °C). The reactor was suspended for 24 h in a circulating glycerol oil bath fitted with a temperature analog controller. The specified temperatures were maintained at 100 ± 0.5 °C by continuously stirring the oil bath as well as the reaction mixture, which was provided with a Teflon-coated magnetic bar.

A gas sample of 0.5 ml was periodically removed from the reaction vessel at the experimental temperature with a pressure series A-2 gas syringe (Dynatech Precision Sampling Corporation). The products were analyzed by gas chromatography in a Perkin–Elmer 8500P chromatograph fitted with a Carbosive S-II column. The reaction vessel was flushed out at the end of the heating time (24 h) and then refilled with CO as described above. This procedure was repeated several times until the rate of H_2 and CO_2 produced and CO consumed was constant.

RESULTS AND DISCUSSION

New complexes with polypyridyl, Rdppz (R = H, Cl, NO_2; Fig. 2) and carbonyl ligands were synthesized by means of a two-step process. In the first step, 1,10-phenanthroline-5,6-dione was reacted with the respective phenylendiamine derivative to obtain the ligands. The ligand was coordinated to the complex precursor $[Ru(CO)_2Cl_2]_n$ in the second step. A series of three new complexes, $[Ru(Rdppz)(CO)_2Cl_2]$, was obtained with R = H (**1**), Cl (**2**), and NO_2 (**3**) (Scheme 1).

Ligand and ruthenium complexes characterization

The ligands and the complexes were characterized by spectroscopic techniques. The IR spectra (KBr) of the polypyridyl ligands show two signals at 1600 and 1574 cm^{-1} corresponding to C=C and C=N stretching modes, respectively. The most important feature in the spectra of the these carbonyl ruthenium complexes is the presence of two signals at 2063–2066 and 2016–1999 cm^{-1}, corresponding to the terminal carbonyl stretching modes of the *cis*-carbonyl, *trans*-chloro type structure (Table 1). The ^{1}H NMR spectra displayed only one signal for the group R—dppz proton H_1,H_2,H_3.[11] The IR and ^{1}H NMR results clearly indicate a *cis*-carbonyl and *trans*-chloro geometry. The other peaks in the IR spectra correspond to the respective Cl—dppz ligand (Fig. 3a) and coordination to the ruthenium complex (Fig. 3b).

Table 1. Stretching frequencies of carbonyl ruthenium complexes

Complexes	ν (cm^{-1}) (CO)
trans-Cl—$[Ru(NO_2dppz)(CO)_2Cl_2]$	2063 and 1999
trans-Cl—$[Ru(Cldppz)(CO)_2Cl_2]$	2065 and 2003
trans-Cl—$[Ru(dppz)(CO)_2Cl_2]$	2066 and 2016

The ^{1}H NMR spectra in $CDCl_3$ for the Cl—dppz and NO_2—dppz ligands display the typical signal pattern for six

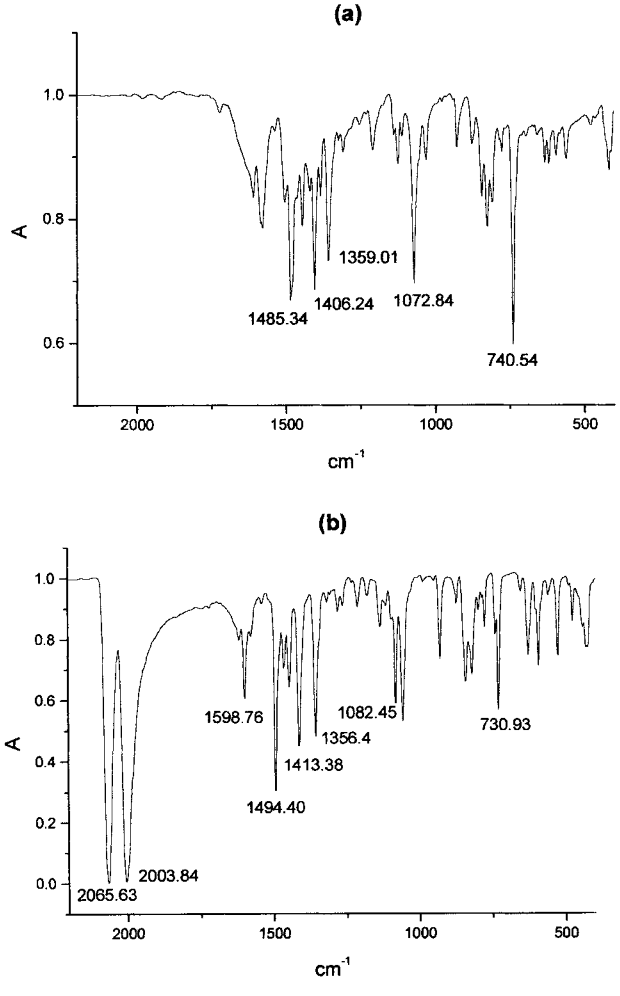


Figure 3. IR spectra for (a) the Cl—dppz ligand and (b) coordination to the ruthenium complex.

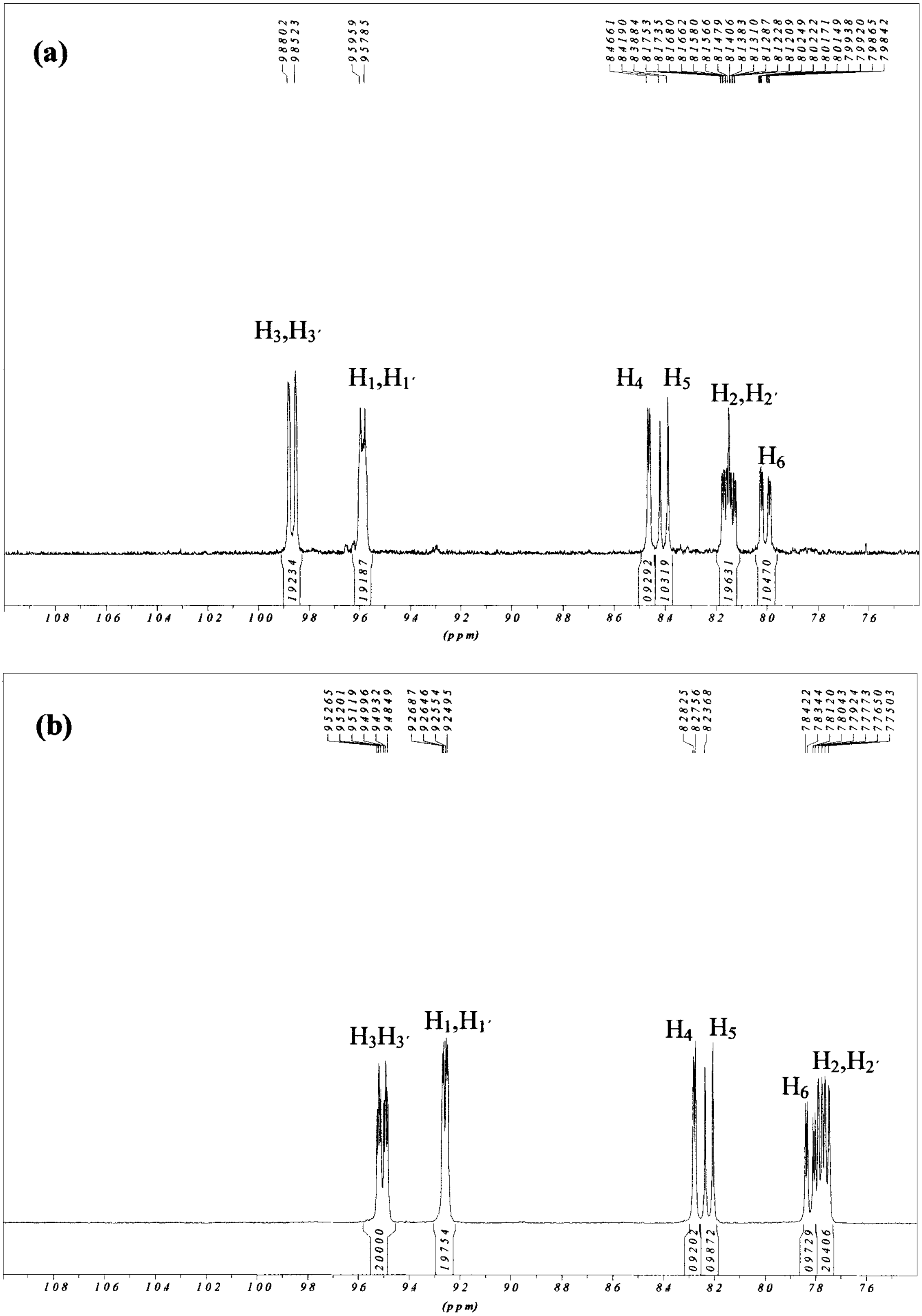


Figure 4. ^{1}H NMR spectra for (a) [Ru(Cl—dppz)(CO)$_2$Cl$_2$] complex and (b) Cl—dppz uncoordinated ligand.

Table 2. WGSR catalytic activity of ruthenium complexes in basic medium under P_{CO} = 0.9 atm at 100 °C[a]

Complexes	$TF(H_2)$[c]	Reference
trans-Cl—[Ru(NO_2dppz)$(CO)_2Cl_2$]	35	This work
trans-Cl—[Ru(Cldppz)$(CO)_2Cl_2$]	28	This work
trans-Cl—Ru(dppz))$(CO)_2Cl_2$	22	This work
trans-Cl—[Ru(bpy*)$(CO)_2Cl_2$][b]	39	21
$Ru_3(CO)_{12}$/2,2 biquinoline	14	This work
$Ru_3(CO)_{12}$/neocuproine	18	18
$Ru_3(CO)_{12}$/1,10-phen	13	18

[a] [Ru] = 0.5 mM, 5.0 ml of 2-ethoxyethanol, 0.54 ml of H_2O and [KOH] = 0.6 M.
[b] bpy* = 4,4′-di-*tert*-butyl-2,2′-bipyridine.
[c] $TF(H_2)$ = moles of H_2/(mol Ru × 24 h).

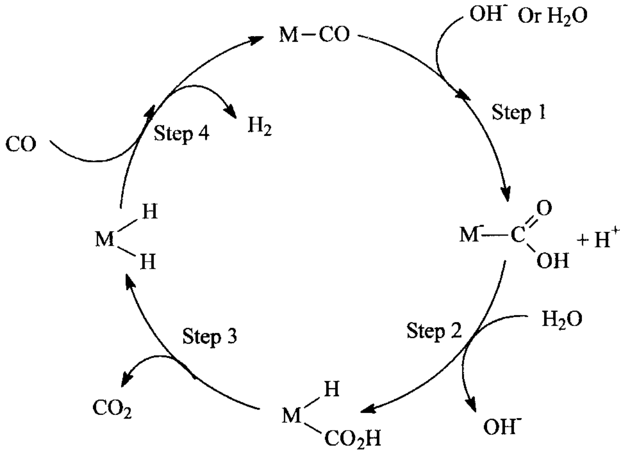
different hydrogen atoms. However, the dppz ligand without substituent shows a spectrum with signals corresponding to five different protons. However, in the [Ru(Rdppz)$(CO)_2Cl_2$] complexes all the signals are localized downfield relative to the uncoordinated ligands. Figure 4 shows the ^{1}H NMR of the Cl—dppz uncoordinated ligand (Fig. 4b) and the [Ru(Cl—dppz)$(CO)_2Cl_2$] complex (Fig. 4a).

Catalytic study of ruthenium complexes in the WGSR

Table 2 summarizes the results of the catalytic activity shown by the new dipyrido[3,2-a:2′,3′-*c*]phenazine—carbonyl ruthenium complexes. Those precursor complexes show good catalytic activity in the WGSR at P_{CO} = 0.9 atm at 100 °C. The H_2 and CO_2 produced with these catalysts are in a 1:1 ratio as required for the WGSR equation ($H_2O + CO = H_2 + CO_2$). The catalytic activity shown for these systems is higher than those previously reported for other ruthenium complexes bearing CO, pyridine or polypyridine ligands under similar reaction conditions.[16] Furthermore, increasing the σ-donor power of the R group causes an increase in the catalytic activity. The Hammet relationship for the [Ru(Rdppz)$(CO)_2Cl_2$] system gives a nonlinear correlation between activity and Hammet parameter.[17] However, this value indicates that the reaction rate is sensitive to the effect of the substituent R, and that confirms the influence of an electronic effect on the catalytic activity.

The new complexes reported here also show better activity than those observed for the ruthenium cluster, $Ru_3(CO)_{12}$, containing 1,10-phenanthroline or neocuproine in the structure.[18] Ishida *et al.*[19] found that the complex [Ru(bpy)$_2$(CO)Cl]PF_6 is active as a catalyst for the WGSR and the turnover number for the H_2 production in the presence of KOH (3.2 mM) is only 3.8 after 20 h, under a CO pressure of 3 atm at 100 °C. The turnover number only increases when the CO pressure is augmented from 5 to 10 atm. Our results show greater activity (TF = 22–35 day^{-1}) under mild conditions (CO pressure of 1 atm and 100 °C).

A mechanism for WGSR catalyzed by soluble ruthenium complexes in a basic medium has been proposed (Scheme 2).[20] In this mechanism the nucleophilic attack on the carbonyl group (step 1) and the steps of formation of a metallic hydride (step 2; step 3) are affected by the high electronic density of the ligand. The increasing electronic density on the metal favors the formation of the mono- and di-hydride species by elimination of OH^- and CO_2 (steps 2 and 3). We have reported recently the activity as catalyst of some ruthenium complexes containing 1,10-phenanthroline or 2,2′-bipyridine as ligand in the WGSR.[21] The 1,10-phenanthroline and 2,2′-bipyridine complexes show that if the electronic density increases on the metal there is better activity in the WGSR (steps 2 and 3; see Scheme 2). Those results also show that an excess of electronic density on the ruthenium center favors the retrodonation on the CO ligand, providing a decrease in the activity (step 1). The activity showed by Ru(dppz)$(CO)_2Cl_2$ and Ru(Rdppz)$(CO)_2Cl_2$ is less than that of Ru(bpy*)(CO)Cl_2 (bpy* = 4,4′-di-*tert*-butyl-2,2′-bipyridine); this result suggests that the formations of the mono- and di-hydride are the determining steps in the proposed mechanism. The decrease of electronic density on the metal is unfavorable to the formation of the mono- and di-hydride (steps 2 and 3). The NO_2—dppz show better activity as a σ-acceptor, suggesting that the *cis*-CO-*trans*-Cl—Ru(NO_2—dppz)$(CO)_2Cl_2$ complexes in the reaction medium produce *cis*-CO-*trans*-Cl—Ru(NH_2—dppz)$(CO)_2Cl_2$. The ruthenium complexes[22] act as a catalyst to convert the NO_2—dppz complex to the corresponding NH_2—dppz complex. The last consideration is supported by IR spectroscopy. The IR spectrum of the *cis*-CO-*trans*-Cl—Ru(NO_2—dppz)$(CO)_2Cl_2$ complex shows two absorptions at around 1562 cm^{-1} and 1344 cm^{-1} corresponding to N—O vibrations. These signals disappear after the catalytic reaction is carried out, being replaced by two new absorptions which appear



Scheme 2.

around 1634 cm^{-1} and 3400 cm^{-1}. These signals are typical for N—H bond vibrations.[23]

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REFERENCES

1. Cole Hamilton DJ. *J. Chem. Soc., Chem. Commun.* 1980; 1213.
2. Ishida M, Tanaka K and Tanaka T. *Organometallics* 1987; **6**: 181.
3. Lehn JM and Ziessel R. *J. Organomet. Chem.* 1990; **382**: 157.
4. Goldstein AS and Drago RS. *J. Chem. Soc., Chem. Commun.* 1991; **21**.
5. Lau CP and Cheng L. *J. Mol. Catal.* 1993; **84**: 39.
6. Kaspar J, Spogliarich R, Mestroni G and Graziani M. *J. Organomet. Chem.* 1981; **208**: C15.
7. Collin JP, Ruppert R and Sauvage JP. *Nouv. J. Chim.* 1985; **9**: 395.
8. Pardey AJ and Ford PC. *J. Mol. Catal.* 1989; **53**: 247.
9. Stemp DA, Holmin RE and Barton JK. *J. Am. Chem. Soc.* 1996; **118**: 5236.
10. Fees J, Kaim W, Moscherosch M, Matheis W, Klima J and Zalis S. *Inorg. Chem.* 1993; **32**: 166.
11. Amouyal E, Homsi A, Chambron JC and Sauvage JP. *J. Chem. Soc., Dalton Trans.* 1990; 1841.
12. López R, Loeb B, Bossie T and Meyer TJ. *Tetrahedron Lett.* 1996; **37**: 5437.
13. Aguirre P, Sariego R and Moya SA. *J. Coord. Chem.* 2001; **54**: 323.
14. Hadda TB, Zidane I, Moya SA and Le Bozec H. *Polyhedron* 1996; **15**: 1571.
15. Ungerman C, Landis V, Moya SA, Cohen H, Walker H, Pearson RG, Rinker RG and Ford PC. *J. Am. Chem. Soc.* 1978; **100**: 4565.
16. Ford PC, Rinker RG, Laine RM, Ungerman C, Landis V and Moya SA. *Adv. Chem. Ser.* 1979; **173**: 81.
17. Lowry TH and Richardson KS. *Mechanism and Theory in Organic Chemistry*. Harper & Row: New York, 1976; 62.
18. Venalainen T, Liskola E, Pakkanen TA and Pakkanen TT. *J. Mol. Catal.* 1986; **34**: 305.
19. Ishida H, Tanaka K, Morimito M and Tanaka T. *Organometallics* 1986; **5**: 724.
20. Urgermann C, Landis V, Moya SA, Cohen H, Walker H, Pearson RG, Rinker RG and Ford PC. *J. Am. Chem. Soc.* 1979; **101**: 5922.
21. Aguirre P, Moya SA, Sariego R, Le Bozec H and Pardey AJ. *Appl. Organomet. Chem.* 2002; **16**: 597.
22. Moya SA, Sariego R, Aguirre P, Sartori R and Dixneuf P. *Bull. Soc. Chim. Belg.* 1995; **104**: 1, 19.
23. Arancibia A, Concepción J, Daire N, Leiva G, Leiva AM, Loeb B, Del Rio R, Diaz R, Francois A and Saldivia M. *J. Coord. Chem.* 2001; **54**: 323.