Pergamon

PII: S0277-5387(97)00130-7

Polyhedron Vol. 16, No. 21, pp. 3847–3850, 1997

0277-5387/97 $17.00+0.00

Complexes with heterocyclic nitrogen ligands—IV: complexes of ruthenium(II) and applications in catalysis

Renato Sariego,* Liliana Farias and Sergio A. Moya

Departamento de Química Aplicada, Facultad de Química y Biología, Universidad de Santiago de Chile, Casillla 40 Santiago 33, Chile

(Received 22 November 1996; accepted 2 April 1997)

Abstract—The synthesis of the new ruthenium(II) complexes $[Ru(NBD)Cl_2L]$ and $[Ru(NBD)ClL(PPh_3)]PF_6$ (where NBD = bicyclo[2.2.1]hepta-2,5-diene, L = 2,2′bipyridine, 1,10-phenanthroline, or some di or tetra methylated 1,10-phenanthroline) is reported. By spectroscopy, the *trans* character of the neutral complexes was deduced. These complexes show catalytic activity in the water gas shift reaction (WGSR) under quite moderate conditions and they are very active catalysts for the hydrogen transfer reactions from isopropanol to acetophenone. © 1997 Elsevier Science Ltd

Keywords: ruthenium; complexes; bipyridine; catalysis; WGSR; hydrogen transfer.

Low oxidation state transition metal complexes containing labile ligands such as the diolefin NBD are good precursors for catalysts in many reactions because substitution may easily allow the coordination of the substrate. The most studied complexes also contain phosphine ligands. The π-acidity of these ligands allows the stabilization of the low oxidation state of the metal, which is normally a condition for the activation of CO for nucleophilic reaction in the WGSR, and also is a condition for the stability of the intermediate hydride in the H transfer reaction [1]. Lately it has become clear that some nitrogen donor ligands are also able to form stable complexes with low oxidation state metals [2]. This is particularly true for those ligands containing sp^2 hybridized nitrogen donors [3]. Many complexes of rhodium(I) are very active in the reactions of small molecules, like CO or H_2 [4], but the value of this metal has steadily increased during the last years, principally because of its success in catalysis. The study of complexes of ruthenium may be useful in this way, because, having many characteristics in common with rhodium, it is considerably cheaper. In this paper, the synthesis and catalytic activity in the WGSR (Eq. 1) and hydrogen transfer reaction (Eq. 2, in which DH is a donor of hydrogen and A is a substrate to be hydrogenated) of some of these complexes is reported

$$CO(g)+H_2O(g) \Leftrightarrow CO_2(g)+H_2(g) \quad (1)$$

$$DH+A \Leftrightarrow D+AH \quad (2)$$

EXPERIMENTAL

Physical Measurements

IR spectra were determined as KBr or polyethylene disk in a Bruker IFS-66V Fourier-transform spectrophotometer. Electronic absorption spectra were obtained on a Shimadzu UV-160 spectrophotometer using different solvents in quartz cells at ambient temperature. Proton NMR spectra of the ligands and the complexes in deuterated chloroform were recorded using a Bruker AC 200 (200 Mz). Conductivity measurements were carried out in anhydrous acetonitrile and chloroform on 10^{-3} M solutions at 25°C using a Cole–Parmer 01481 conductivity meter. Electrochemical measurements were carried out on a classical three-electron potentiostatic set-up consisting of a Bank–Wenking POS 73 potentiostat, an XY Linseis recorder model OS 17100 and a Gould oscilloscope model OS 4100. Working and auxiliary electrode were a Pt disk electrode and a Pt wire,

* Author to whom correspondence should be addressed.

respectively. The reference electrode (an aqueous saturate sodium chloride calomel) was connected to the cell by a Vycor bridge (porous glass N° 7930) filled with the corresponding solvent and supporting electrolyte. A 0.1 mol L^{-1} solution of purified and dried tetrabutylammonium perchlorate (TBAP) in acetonitrile or methylene chloride was used as supporting electrolyte. The reference electrode was calibrated against Cp_2Fe, which was used as the reference in this work. The separation between the anodic and the cathodic peaks for the Cp_2Fe oxidation was 80–85 mV in acetonitrile.

Microanalyses were performed by the Facultad de Ciencias Químicas y Farmaceuticas (Universidad de Chile). The catalytic studies on the WGSR were carried out following the methods and apparatus reported in the literature [5]. The H_2 produced in the WGSR was analyzed by GC in a Perkin–Elmer 8500 GC, with a Carbosieve SII column. The batch reactor was charged with 0.9 atm of CO and heated at 100°C. The hydrogen transfer reaction were carried out as previously reported [6] in 2-propanol using sodium isopropoxyde as base. The reaction was followed by GC in a Perkin–Elmer Sigma 3 GC, equipped with a SP-1000 column.

Materials

$RuCl_3 \cdot 3H_2O$, bicyclo[2.2.1]hepta-2,5-diene(NBD), 2,2-bipyridine (bpy), 1,10-phenanthroline (phen), 5,6-dimethyl-1,10-phenanthroline (5,6-DM-phen), 4,7-dimethyl-1,10-phenanthroline (4,7-DM-phen), 3,4,7,8-tetramethyl-1,10-phenanthroline (TM-phen), silver hexafluorophosphate and triphenylphosphine from Aldrich, were used as received. $[Ru(NBD)Cl_2]_n$ was prepared as reported [7].

The neutral complexes were prepared by the following general method. To a stirred suspension of the polymer $[Ru(NBD)Cl_2]_n$ (264.1 mg, 10^{-3} formula weight) in acetone (100 cm^3) under nitrogen and at room temperature, 1 mmol of the ligand was added. After 20–24 h a dark red color of the suspension indicated the end of the reaction. After filtration, the solid was partially dissolved in chloroform, the separated solution was concentrated and precipitated with ethyl ether. All the complexes were light yellow and presented molar conductivity in dichloromethane and in acetonitrile around zero.

The cationic complex, $[Ru(NBD)Cl(phen)PPh_3]PF_6$, was obtained by the following method. $Ru(NBD)Cl_2(phen)$ (222.2 mg, 0.5 mmol), PPh_3 (131.2 mg, 0.5 mmol) and $AgPF_6$ (126.4 mg, 0.5 mmol) in CH_2Cl_2 (80 cm^3) were stirred under argon, protected from the light, for 45 min at room temperature. The AgCl formed was separated by filtration and the solution evaporated to dryness. The solid was washed with ethyl ether to take out unreacted PPh_3. Unreacted neutral complex was separated by dissolving the cationic product in acetone. The solid obtained after evaporating to dryness the acetone solution was recrystallized from dichloromethane with ether.

1. $Ru(NBD)Cl_2(bpy)$, was obtained in 48% yield. m.p. 220°C (d). IR (KBr): ν(C—N) 1599.7 cm^{-1}, ν(C=C) 1420.7 cm^{-1}, ν(Ru–olefin) 261.9 cm^{-1}, ν(Ru—N) 367.6 cm^{-1}, ν(Ru—Cl) 352–331.5 cm^{-1}. Anal. Found: C, 48.7; H, 3.8; N, 6.6. Calc. for $RuCl_2N_2C_{17}H_{16}$: C, 48.6; H, 3.8; N, 6.7%.

2. $Ru(NBD)Cl_2(phen)$, was obtained in 54% yield. m.p. 215°C (d). IR (KBr) ν(C—N) 1513.0 cm^{-1}, ν(C=C) 1424.9 cm^{-1}, ν(Ru–olefin) 263.8 cm^{-1}, ν(Ru—N) and ν(Ru—Cl) 353–334.2 cm^{-1}. Anal. Found: C, 51.6; H, 3.5; N, 6.3. Calc. for $RuCl_2N_2C_{19}H_{16}$: C, 51.4; H, 3.6; N, 6.3%.

3. $Ru(NBD)Cl_2(5,6\text{-DM-phen})$, was obtained in 33% yield. m.p. 245°C (d). IR (KBr): ν(C—N) 1513.7 cm^{-1}, ν(C=C) 1421.0 cm^{-1} ν(Ru–olefin) 256.7 cm^{-1}, ν(Ru—N) 368.5 cm^{-1}, ν(Ru—Cl) 355–336.3 cm^{-1}. Anal. Found: C, 50.2; H, 4.0; N, 5.4 Calc. for $RuCl_2N_2C_{21}H_{20}$: C, 53.4; H, 4.3; N, 5.9%.

4. $Ru(NBD)Cl_2(4,7\text{-DM-phen})$, was obtained in 55% yield. m.p. 238°C (d). IR (Kbr): ν(C—N) 1518.7 cm^{-1}, ν(C=C) 1421.5 cm^{-1} ν(Ru–olefin) 262.6 cm^{-1}, ν(Ru—N) 363–312 cm^{-1}, ν(Ru—Cl) 356–341.6 cm^{-1}. Anal. Found: C, 50.9; H, 4.0; N, 5.6. Calc. for $RuCl_2N_2C_{21}H_{20}$: C, 53.4; H, 4.3; N, 5.9%.

5. $Ru(NBD)Cl_2(TM\text{-phen})$, was obtained in 58% yield. m.p. 245°C (d). IR (KBr): ν(C—N) 1523.9 cm^{-1}, ν(C=C) 1426.8 cm^{-1}, ν(Ru–olefin) 257.9 cm^{-1}, ν(Ru—N) 367–328 cm^{-1}, ν(Ru—Cl) 339 cm^{-1}. Anal. Found: C, 55.1; H, 4.88; N, 5.6. Calc. for $RuCl_2N_2C_{23}H_{24}$: C, 55.2; H, 4.8; N, 5.6%.

6. $[Ru(NBD)Cl(phen)PPh_3]PF_6$, was obtained in 17% yield. m.p. 160°C (d). IR (KBr): ν(C—N) 1514.8 cm^{-1}, ν(C=C) 1434.5 cm^{-1}, ν(Ru–olefin) 269.8 cm^{-1}, ν(Ru—N) 353–305 cm^{-1}, ν(Ru—Cl) 334 cm^{-1}. Anal. Found: C, 53.2; H, 3.7; N, 2.4. Calc. for $RuClN_2C_{37}H_{31}P_2F_5$: C, 54.5; H, 3.8; N, 3.4%.

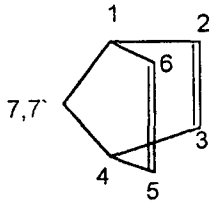
RESULTS AND DISCUSSION

The reaction of the polymer $[Ru(NBD)Cl_2]_n$ with bpy or the phenanthroline derivatives afforded the neutral complexes $Rh(NBD)Cl_2L$ in moderate yield. Their formulation is supported by the elemental analysis and molar conductivity. Coordination of the ligands is revealed by the displacement to low energy of the stretching modes of C=C of the free diolefin and the C—N of the free nitrogen donor ligands in the complexes [8,9]. The low energy bands corresponding to the Ru–olefin [10], Ru—N and Ru—Cl stretching bands appear in the same region of the spectra, nevertheless it was possible to distinguish any one in all the cases except when the ligand was phen. In all the complexes they were assigned to structures in which the Cl ligands are in the *trans* position [11]. The ^1H NMR (Tables 1 and 2) give support to this assumption. The spectra show signals for the NBD

Table 1. ^{1}H NMR data in free and coordinated NBD[a]

Compound	NBD protons[b]		
	$H_{1,4}$	$H_{2,3,5,6}$	$H_{7,7}$
NBD	3.55 m	6.70 t	2.00 t
[Ru(NBD)Cl_2(bipy)]	4.06 m	5.00 t	1.62 t
[Ru(NBD)Cl_2(phen)]	4.13 m	5.15 t	1.62 t
[Ru(NBD)Cl_2(5,6-DM-phen)]	4.14 m	5.13 t	1.67 t
[Ru(NBD)Cl_2(4,7-DM-phen)]	4.12 m	5.11 t	1.66 t
[Ru(NBD)Cl_2(TM-phen)]	4.12 m	5.11 t	1.66 t
[Ru(NBD)Cl(phen)(PPh_3)]PF_6	4.05 m	5.12 t	1.63 t

[a] Shift are in ppm from TMS, $CDCl_3$-d_1.
[b] The protons are assigned as follows.



and nitrogen donor ligand, slightly affected by the coordination, which integrate well for a 1 : 1 ratio of both ligands in the complexes. Furthermore, their mutual interactions are practically restricted only to the shift to higher field of the H_2 and H_9 of the pyridinic ligand, affected by the magnetic current of the double bonds of the *trans* coordinated NBD ligand, and also by the release of the interaction with the lone pair of electrons in the N of the free ligand (Table 2). On the other hand, the equivalent of the ^{1}H NMR signals of the two moieties of the N donor ligands indicate the coordination by both N donor atoms.

The electronic spectra of the complexes confirm the coordination of the ligands, as their characteristic intraligand transitions, slightly shifted to high or low energy, are observed. The classical CT characteristic of $[Ru(bpy)_3]^{2+}$, $[Ru(phen)_3]^{2+}$, $[Ru(bpy)_2(PPh_3)_2]^{2+}$, $[RuL_3]^{2+}$ (L = phen, 5,6-DM-phen, 4,7-DM-phen and TM-phen) all appear between 420 and 450 nm. The complexes here reported show this CT bands at higher energy (360–380 nm) probably because of the stabilization of the $d\pi$ orbitals after coordination of the NBD π acid ligand [12]. Cyclic voltammetry of the neutral complexes confirm the oxidation state of Ru^{II} as only one reversible one-electron oxidation wave was possible to observe in the anodic region centered around 0.57 V. The methyl substitution in the phenantroline ligand produce a slight stabilization of the Ru^{III} state. All the neutral complexes also show an irreversible reduction wave which can be centered in the ligand [13]. On the other hand, the cationic complex show four irreversible oxidation peaks.

All the complexes are active catalysts in the WGSR (Eq. 1 and Table 3). As has been generally observed, the activity of the neutral complexes increases with the basicity of the medium until a maximum at a ratio [base]/[catalyst] of around 10. At larger base concentration, KOH or NEt_3, progressive decomposition of the complex was observed to an insoluble product and consequently a reduction of their activity. The cationic complex is more sensitive to decomposition by bases, so the reported activity in this case corresponds to experiments without the addition of base (Table 3). The substitution for methyl groups

Table 2. ^{1}H NMR data in free and coordinated ligands[a]

Compound	Ligand protons[b]				
	$H_{2,9}$	$H_{3,8}$	$H_{4,7}$	$H_{5,6}$	CH_3
[Ru(NBD)Cl_2(bipy)]	8.12 m	7.43 dd	7.94 m	7.94 m	—
[Ru(NBD)Cl_2(phen)]	8.41 dd	7.75 dd	8.34 dd	7.95 s	—
free phen	9.19 dd	7.63 dd	8.24 dd	7.79 s	
[Ru(NBD)Cl_2(5,6-DM-phen)]	8.55 dd	7.74 dd	8.26 dd	—	2.78 s
free 5,6-DM-phen	9.14 dd	7.65 dd	8.45 dd		2.73 s
[Ru(NBD)Cl_2(4,7-DM-phen)]	8.18 dd	7.55 d	—	8.09 s	2.86 s
free 4,7-DM-phen	9.05 dd	7.46 dd		8.03 s	2.80 d
[Ru(NBD)Cl_2(TM-phen)]	8.07 s	—	—	8.03 s	2.46, 2.78 s
free TM-phen	8.89 s			8.01 s	2.52, 2.67 s
[Ru(NBD)Cl(phen)(PPh_3)]$^+$	8.39 dd	7.71 dd	8.29 dd	7.93 s	—

[a] Shift are in ppm from TMS, $CDCl_3$-d_1.
[b] Protons are assigned as follows:

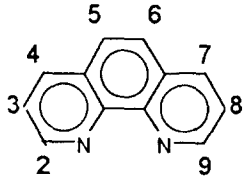


Table 3. Catalytic activity in the WGSR

Complex	Turnover/day[a]
[Ru(NBD)Cl_2(bipy)]	22
[Ru(NBD)Cl_2(phen)]	32
[Ru(NBD)Cl_2(5,6-DM-phen)]	37
[Ru(NBD)Cl_2(4,7-DM-phen)]	13
[Ru(NBD)Cl_2(TM-phen)]	7
[Ru(NBD)Cl(phen)(PPh_3)]PF_6[b]	28

[a]complex 7×10^{-4} M in etoxyethanol, [KOH]/[Complex] = 10, P_{CO} = 0,92 atm. y T = 100°C.
[b]Without KOH.

in the phenanthroline ligands increases the electronic density on the metal, making more difficult the nucleophilic attack of the OH^- on a coordinated carbonyl, which is assumed to be previously formed by substitution of the labile NBD ligand in the CO environment. This is believed to be the rate-limiting step in this kind of reactions.

The hydrogen transfer reaction from isopropanol to acetophenone (Eq. 2, A = acetophenone) is very strongly catalyzed by the neutral complexes (Fig. 1). Practically no effect of the methyl groups of the phenanthroline ligands on their activity was observed, but the concentration of the base was very important until about 2.5 times the concentration of the neutral complex. The formation of metal hydrides it is assumed in this case, as has been reported for $RuCl_2PPh_3$ complexes under similar conditions

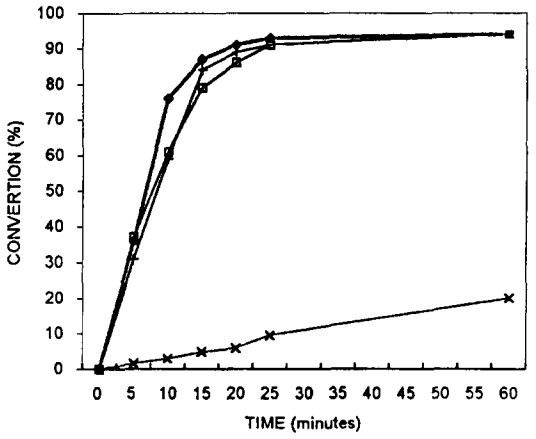


Fig. 1. Catalytic activity of the complexes [Ru(NBD)Cl_2(Phen)] □, [Ru(NBD)Cl_2(4,7-DM-Phen)] +, [Ru(NBD)Cl_2(TM-Phen)] ◇and [Ru(NBD)Cl(Phen)(PPh_3)PF_6 × in the hydrogen transfer reactions from 2-propanol to acetophenone.

[14,15]. Another equivalent of base will substitute the product of the reaction (1-phenylethanol) in the complex. The lability of the NBD ligand may also have a role in the catalytic cycle, providing additional coordination site to a β hydrogen transfer and to coordinate the ketone substrate.

These complexes were also active catalysts of the hydrogen transfer reaction to cyclohexene and 1-hexene, the most basic ligand (tetramethyl phenanthroline) giving rise to the most active catalyst. In the case of 1-hexene, a large isomerization to internal isomers was observed at the beginning of the reaction. Later on these products were also hydrogenated. Benzaldehyde and nitrobenzene were not hydrogenated under these conditions.

Acknowledgements—We are grateful to DICYT (Universidad de Santiago de Chile) and FONDECYT-CHILE (Proyecto 1941105) for their support on this research.

REFERENCES

1. Laine, R. M., Crawford, E. J., *J. Mol. Catal.*, 1988, **44,** 357.
2. Moya, S. A., Pastene, R., Sariego, R., Sartori, R., Aguirre, P, Le Bozec, H., *Polyhedron*, 1996, **15,** 1823.
3. Togni, A., Venanzi, L. M., *Angew. Chem. Int. Ed. Engl.*, 1994, **33,** 497.
4. Chaloner, P. A., Esteruelas, M. A., Joó, F., Oro, L. A., *Homogeneous Hydrogenation*, Kluwer Academic, Dordrecht (1993).
5. Ungermann, C., Landis, V., Moya, S. A., Cohen, H., Walker, H., Pearson, R. G., Rinker, R. G., Ford, P. C., *J. Am. Chem. Soc.*, 1979, **101,** 5922.
6. Sariego, R., Carkovic, I., Martinez, M., Valderrama, M., *Trans. Met. Chem.*, 1984, **9,** 106.
7. Abel, E. W., Bennet, M. A., Wilkinson, G., *J. Chem. Soc. Dalton Trans*, 1959, 3178.
8. Adams, D. M., Fernando, W. S., *Inorg. Chim. Act*, 1973, **7,** 277.
9. Brown, G. M., Weaver, T. R., Keene, F. R., Meyer, T. J., *Inorg. Chem.*, 1976, **15,** 190.
10. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Ed, Wiley Interscience, New York (1986).
11. Evans, Y. P., Spencer, A., Wilkinson, G., *J. Chem. Soc., Dalton Trans.*, 1973, 204.
12. Sullivan, B. P., Baumann, J. A., Meyer, T. J., Salmon, D. J., Lehmann, H., Laudi, A., *J. Am. Chem. Soc.*, 1977, **99,** 7378.
13. Matsumara-Inoue, T., Ikemato, Y., Umezawa, Y., *J. Electroanal. Chem.*, 1986, **209,** 135.
14. Crabtree, R. H., Mellea, M. F., Mihelcic, J. M., Quirk, J. M., *J. Am. Chem. Soc.*, 1982, **104,** 107.
15. Esteruelas, M. A., Sola, E., Oro, L. A., Werner, H., Meyer, J., *J. Mol. Catal.*, 1988, **45,** 1.