APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 272–276
Materials, Nanoscience and Catalysis **AOC**
Published online 19 December 2005 in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.1021

New polynuclear carbonyl ruthenium (II) complexes derived from 1,8-naphthyridine

Juana Gajardo[1], Juan C. Araya[1], Sergio A. Moya[1]*, Alvaro J. Pardey[2], Veroniqué Guerchais[3], Hubert Le Bozec[3] and Pedro Aguirre[4]*

[1]Universidad de Santiago de Chile, Facultad de Química y Biología, Av. Libertador Bernardo O'Higgins 3363, Casilla 40, Correo 33, Santiago, Chile
[2]Universidad Central de Venezuela, Facultad de Ciencias, Caracas, Venezuela
[3]Université de Rennes I. Organomet. et Cat. C. de Beaulieu, Rennes, France
[4]Universidad de Chile, Facultad de Ciencias Químicas y Farmacéuticas, Casilla 233, Santiago, Chile

Received 18 May 2005; Accepted 17 October 2005

This work shows the synthesis and characterization of new carbonyl complexes derived of 1,8-naphthyridine. Covalently bonded complex can be successfully employed in building of supramolecular structures. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: ruthenium complexes; 1,8-naphthyridine

INTRODUCTION

The synthesis and properties of polypyridine complexes of ruthenium have been extensively studied, particularly those containing the ligand 2,2′-bipyridine and 1,10-phenanthroline. Ruthenium polypyridine complexes are of great interest because of their redox properties and metal-to-ligand charge transfer (MLCT) energies.[1,2] The ligand dipyrido[3,2-a:2,3-c]phenazine coordinated to a metal center could have interesting properties that might affect the catalytic activities in water gas shift reaction.[3]

Naphthyridine derivatives show an interesting behavior in photoelectric converter application. This photoelectrochemical cell is prepared using metals like ruthenium, osmium, iron and copper, where the semiconductor is preferably TiO_2.[4]

Naphthyridine derivatives can be prepared via a Friedländer condensation of 2-aminonicotinaldehyde (**1**) and an enolizable ketone. The reaction occurs with the liberation of two water molecules for each pyridine ring formed.[5,6] If the ketone has a substituent R, a 1,8-naphthyridine substituted in the 2 position is obtained, as shown in Scheme 1 (R is frequently an aromatic substituent).

On the other hand, ruthenium polypyridines have been widely studied because of their activity in the water gas shift reaction (WGSR)[1,2,7–10] and in the reduction of CO_2.[11–13,15] Also, both [$Ru_3(CO)_{12}$–2,2′-bipyridine] and [$Ru_3(CO)_{12}$–2,2′-bipyridine–SiO_2] systems have been found to be active in 1-hexene hydroformylation.[16] The cluster precursor system [$Ru_3(CO)_{12}$–2,2′-bipyridine–SiO_2] is also highly active in the WGSR.[17]

Based on these antecedents, we introduce the synthesis of multimetallic ruthenium carbonyl complexes derived from 1,8-naphthyridine and their potential application in homogeneous catalysis.

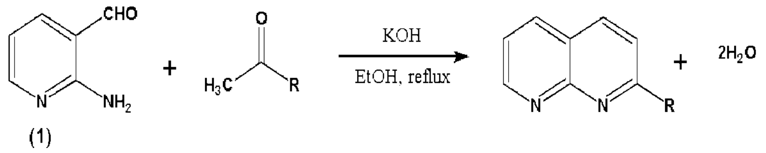
RESULTS AND DISCUSSION

Condensation of 1,3,5-triacetylbenzene with **1** produces the new ligand 1,3,5-tri(1,8-naphthyridine-2-yl)benzene (TNB) (Scheme 1). Similarly, condensation using 1,4-diacetylbenzene and 2,6-diacetylpyridine leads to the formation of the new ligand 1,4-di(1,8-naphthyridine-2-yl)benzene (DNB). The 2,6-di(1,8-naphthyridine-2-yl)pyridine (DNP) ligand was prepared by a variation of the procedure suggested by Thummel[18] (Scheme 2).

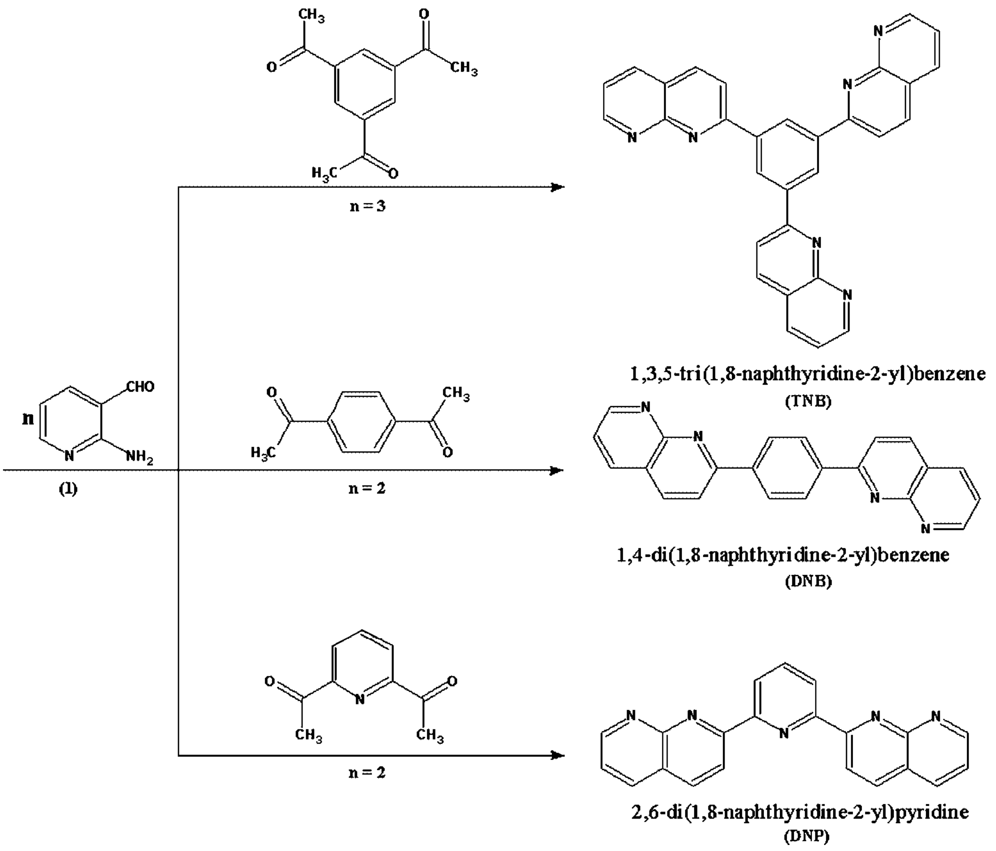
The ^{1}H-NMR spectra of the new ligands shows the characteristic signals for a substituted naphthyridine in the 2 position.[19] The typical signal at low field, for hydrogen 1, is split as a doublet of doublets with coupling constants, *J*, of 1.9

---

*Correspondence to: Pedro Aguirre, Universidad de Chile, Facultad de Ciencias Químicas y Farmacéuticas, Casilla 233, Santiago, Chile.
E-mail: Paguirre@ciq.uchile.cl or to Sergio A. Moya, Universidad de Santiago de Chile, Facultad de Química y Biología, Av. Liberatador Bernardo O'Higgins 3363, Casilla 40, Correo 33, Santiago, Chile.
E-mail: smoya@lauca.usach.cl
Contract/grant sponsor: Fondecyt-Chile; Contract/grant number: 1050168.



Scheme 1.



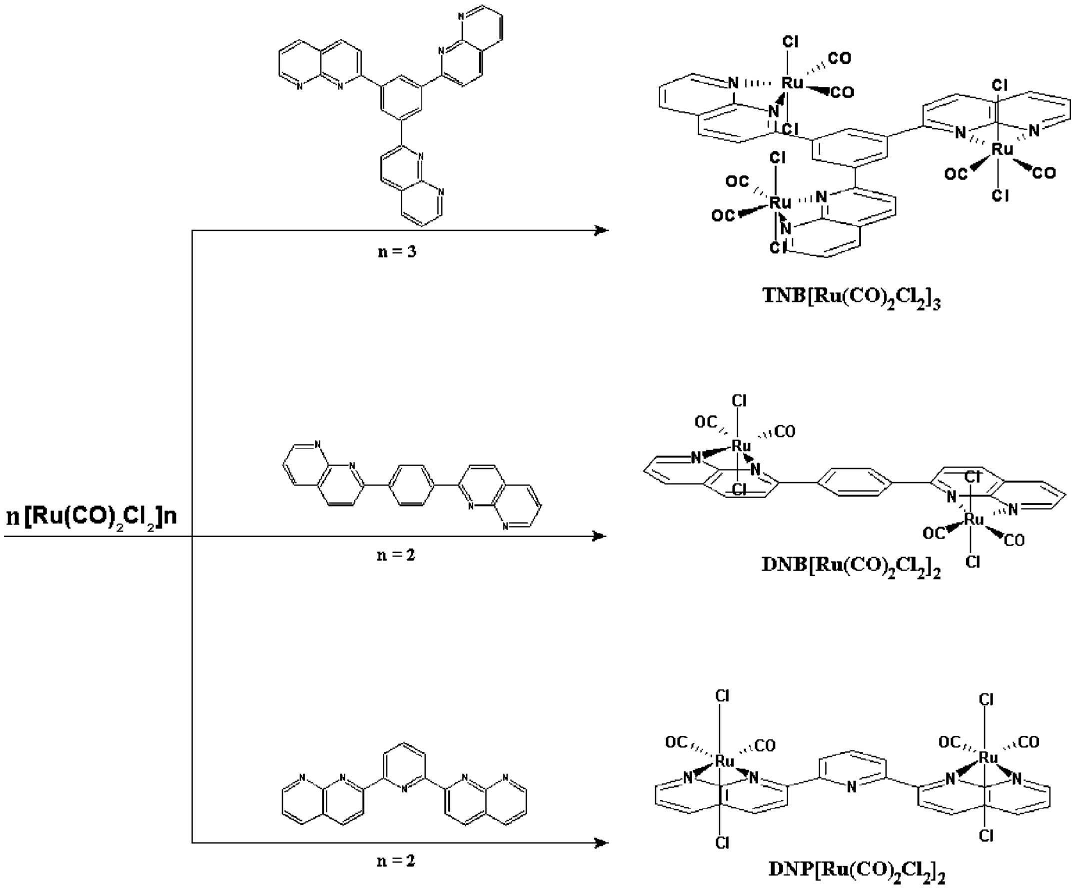
Scheme 2.

and 4.2 Hz. Hydrogens 4 and 5, as a consequence of their coupling, exhibit two doublets separated by a *J* of 8.5 Hz. Hydrogens 2 and 3 appear as doublets of doublets, coupling between them and with hydrogen 1, having coupling constants of 8.1 and 1.9 Hz, respectively. Although the ^{1}H-NMR spectrum for the 1,4-di(1,8-naphthyridine-2-yl)benzene compound is very similar, there are some differences. For example, the signal for hydrogen 4 appears shifted to δ 8.15 compared with δ 8.53 for the 1,3,5-tri(1,8-naphthyridine-2-yl)benzene case. The chemical shift for the hydrogen of the central benzene ring is different (δ 8.54 for DNB and 9.56 for TNB). These differences in the chemical shifts are the consequence of typical anisotropy relative to the central ring.

The ^{1}H-NMR spectrum of 2,6-di(1,8-naphthyridine-2-yl)pyridine shows a similar pattern, having the influence of the pyridine central ring. The similar chemical environment of the protons for the 2,6 disubstituted pyridine and the naphthyridine is responsible for the signals for protons 5 and 6 overlapping.

The proposed structure of the new ligands has been confirmed by ^{13}C-NMR and ^{1}H-^{13}C HMQC spectroscopy. This NMR analysis confirms the pattern of signals for each one of the ligands.

In addition, elemental analysis gives the correct proportion of the elements forming the molecule. The possibility of coordinating more than one metal to these ligands provides the opportunity to prepare complexes with different numbers of metal centers. On the other hand, using different metals, the possibility of generating polymetallic and heteronuclear complexes increases. Considering the previous statements, excess of precursor $[Ru(CO)_2Cl_2]_n$ was used to generate the respective trimetallic complexes with TNB and bimetallic complexes with DNP and DNB ligands, respectively (Scheme 3).



Scheme 3.

The new complexes are scarcely soluble in most of the solvents. However, they are soluble enough to allow spectroscopical characterization. The ^{1}H-NMR spectra of the complexes are very similar to those shown by the uncoordinated ligands, with the expected shift of the ligand signals to lower field, as a consequence of the coordination to the ruthenium centers. It is interesting to indicate for the complex derived from DNP that there is no presence of any isomer for the complex, which could be possible by the coordination of one metal center with the pyridine nitrogen atom and one naphthyridine nitrogen. The spectroscopic characterization of the formed complexes becomes easier in those cases where the complex is symmetrical.

The IR spectra of the complexes show the coordination of the metal, providing typical signals for the terminal dicarbonyl complexes. The signals observed for ν-CO indicate a *cis*-CO–*trans*-Cl configuration for the complex containing the 1,8-naphthyridine ligand. We have previously reported the synthesis of a similar compound where it is possible to observe that the *cis*-CO–*cis*-Cl isomer shows two signals between 2000 and 1980 cm^{-1}, which correspond to the *cis*-CO configuration. In the presence of a deuterated coordinating solvent (acetonitrile or dimethylsulfoxide), the symmetry of the *cis*-CO–*trans*-Cl–DNP[Ru(CO)$_2$Cl$_2$]$_2$ complex is lost after some reaction time, duplicating the pattern of signals observed in CDCl$_3$. The change in the observed signals agrees well with an initial *cis*-CO–*trans*-Cl symmetry for the complex, which has also been confirmed by other authors.[14]

Figure 1 shows the ^{1}H-NMR spectra of the free ligand DNP in DMSO-d$_6$ (top) and the ^{1}H-NMR spectra of their bimetallic complex DNP[Ru(CO)$_2$Cl$_2$]$_2$ in DMSO-d$_6$ (bottom). One of the problems that has to be overcome is the low solubility shown by these complexes. In order to improve the solubility we are working on the formation of more soluble cationic species.

EXPERIMENTAL

1,3,5-Tris(1,8-naphthyridine-2-yl) benzene (TNB)

A mixture of **1** (500 mg; 4.10 mmol) and 1,3,5-triacetylbenzene (279 mg; 1.37 mmol), ethanol saturated with KOH (3 ml), in absolute ethanol (50 ml) was refluxed for 1.5 h under nitrogen. After the system had cooled, a solid was separated by filtration as a yellow-white solid. After recrystallization from chloroform, a pale yellow solid was obtained (492 mg; 1.07 mmol); yield, 78%; m.p. 300 °C (d). ^{1}H-NMR (300 MHz,

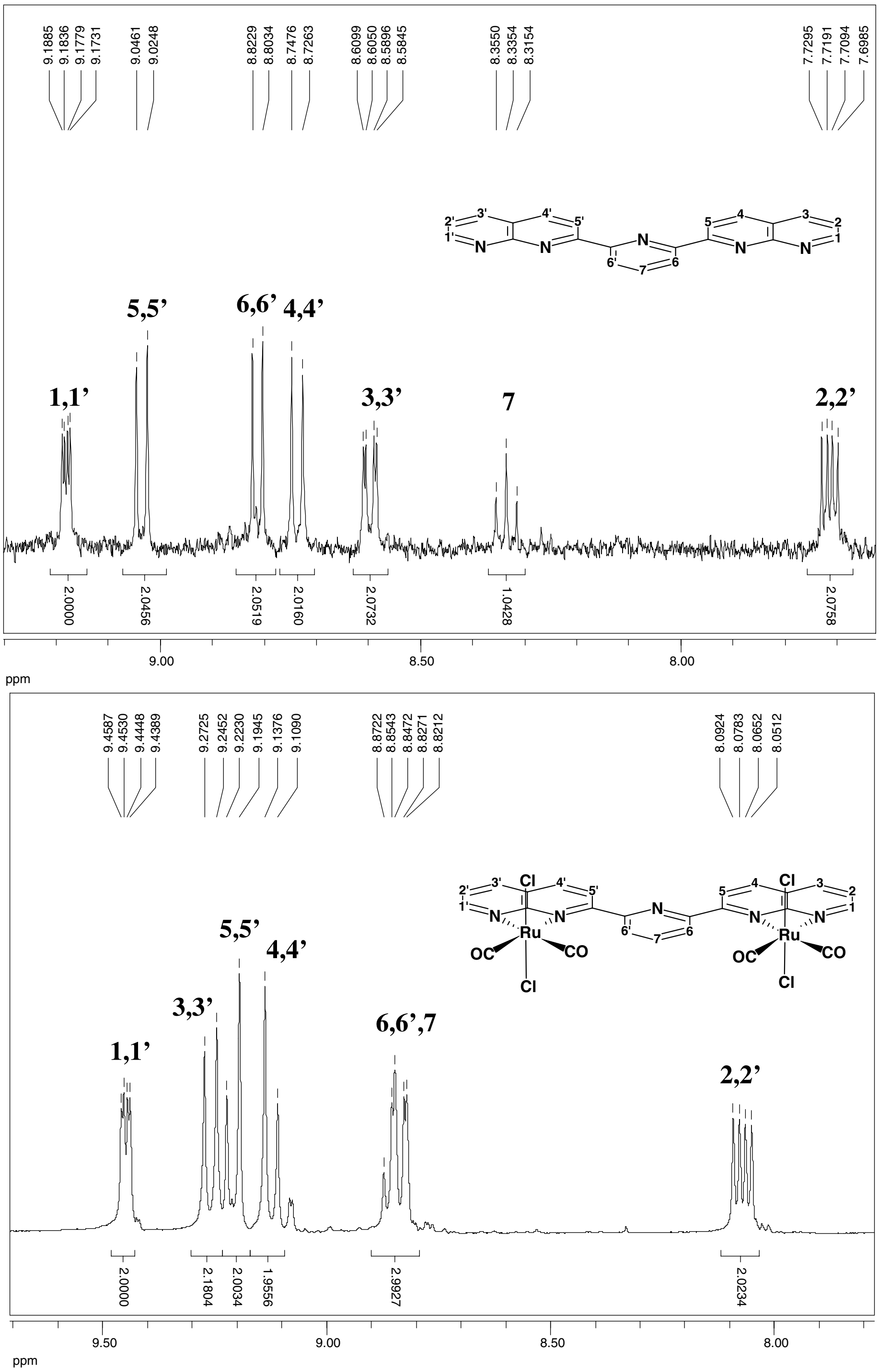


Figure 1. ^{1}H-NMR spectra for DNP[Ru(CO)$_2$Cl$_2$]$_2$ complex (bottom) and uncoordinated ligand (top).

CDCl$_3$)δ 9.56 (s, 3H), 9.22 (dd, 3H, $J = 4.2, 1.9$ Hz), 8.53 (d, 3H, $J = 8.5$ Hz), 8.40 (dd, 3H, $J = 8.5$ Hz), 8.31 (dd, 3H, $J = 8.1, 1.9$ Hz), 7.56 (dd, 3H, $J = 8.1, 4.2$ Hz). ^{13}C RMN (CDCl$_3$, 75 MHz) δ 158.54, 155.10, 152.92, 138.70, 136.94, 135.97, 127.88, 121.17, 120.97, 119.58. Anal. calcd for $C_{30}H_{18}N_6 \cdot 1.25H_2O$ (%): C, 74.30; H, 4.26; N, 17.32. Found (%): C, 74.22; H, 3.85; N, 17.20.

1,4-Bis(1,8-naphthyridine-2-yl)benzene (DNB)

A mixture of **1** (500 mg; 4.10 mmol), 1,4-diacetylbenzene (332 mg; 2.05 mmol) and ethanol saturated with KOH (3 ml), in 50 ml of absolute ethanol, was heated at 50 °C for 3 h and then it was refluxed at 90 °C for 18 h under nitrogen. The brown solid formed was filtered and recrystallized from chloroform to yield a white solid (583 mg; 1.75 mmol); yield, 85%; m.p., 324 °C (d). ^{1}H-RMN (300 MHz, $CDCl_3$) δ 9.18 (dd, 2H, $J = 4.2$, 1.9 Hz), 8.54 (s, 4H), 8.32 (d, 2H, $J = 8.5$ Hz), 8.24 (dd, 2H, $J = 8.1$, 1.9 Hz), 8.15 (d, 2H, $J = 8.5$ Hz), 7.51 (dd, 2H, $J = 8.1$, 4.2 Hz). ^{13}C RMN ($CDCl_3$, 75 MHz) δ 159.55, 156.22 154.05, 139.90, 137.91, 136.79, 128.37, 121.98, 121.95, 119.81. Anal. calcd for $C_{22}H_{14}N_4$ (%): C, 79.03; H, 4.22; N, 16.75. Found (%): C, 78.83; H, 4.04; N, 16.80.

2,6-Bis(1,8-naphthyridine-2-yl)pyridine (DNP)

A mixture of **1** (500 mg; 4.10 mmol), 2,6-diacetylpyridine (335 mg; 2.05 mmol) and ethanol saturated with KOH (3 ml), in absolute ethanol (50 ml), was refluxed for 24 h under nitrogen. The product was recovered by filtration and after recrystallization from chloroform a bright yellow solid was obtained (667 mg; 1.99 mmol); yield, 62%; m.p., 310 °C (d). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.25 (dd, 2H, $J = 4.2$, 2.0 Hz), 9.07 (m, 4H, overlapped), 8.46 (d, 2H, $J = 8.5$ Hz), 8.34 (dd, 2H, $J = 2.0$, 8.1 Hz), 8.19 (t, 1H, $J = 8.1$ Hz), 7.60 (dd, 2H, $J = 4.2$, 8.1 Hz). ^{1}H-NMR (400 MHz, DMSO-d_6) δ 9.18 (dd, 2H, $J = 4.2$; 2.0 Hz), 9.04 (d, 2H, $J = 8.5$ Hz), 8.81 (d, 2H, $J = 7.9$ Hz), 8.74 (d, 2H, $J = 8.5$ Hz), 8.60 (dd, 2H, $J = 8.2$; 2.0 Hz), 8.33 (t, 1H, $J = 7.9$ Hz), 7.71 (dd, 2H, $J = 8.2$; 4.2 Hz). MS, $m/z = 335$ (100%, $C_{21}H_{13}N_5^+$). Anal. calcd for $C_{21}H_{13}N_5 \cdot 0.5H_2O$ (%): C, 73.25; H, 4.10; N, 20.33. Found (%): C, 73.73; H, 3.77; N, 20.42.

TNB[Ru(CO)$_2$Cl$_2$]$_3$

A mixture of TNB (250 mg; 0.54 mmol) and $[Ru(CO)_2Cl_2]_n$ in excess ethanol was refluxed for 6 h under nitrogen. The product was obtained by filtration, washed with hot ethanol and recrystallized from chloroform. The trimetallic complex was obtained as a pink solid (450 mg; 0.40 mmol); yield, 74%; m.p., 260 °C (d). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 10.10 (dd, 3H, $J = 1.8$, 4.2 Hz), 8.96 (s, 3H), 8.67 (d, 3H, $J = 8.2$ Hz), 8.65 (d, 3H, $J = 8.5$ Hz), 8.27 (d, 3H, $J = 8.5$ Hz), 7.88 (dd, 3H, $J = 4.2$, 8.2 Hz). The ^{1}H-NMR spectrum corresponds to the major isomer. IR (KBr), νCO 1981.2; 2040.4; 2136.5 cm^{-1}.

Anal. calcd for $C_{36}H_{18}N_6O_6Cl_6Ru_3$ C, 37.68; H, 1.57; N, 7.33. Found C, 37.75; H, 2.08; N, 7.54. Calculated (%) for H, 1.60; N, 7.33. Found (%) for H, 2.08 and N, 7.54.

DNB[Ru(CO)$_2$Cl$_2$]$_2$

A mixture of DNB (250 mg; 0.75 mmol) and $[Ru(CO)_2Cl_2]_n$ (excess) in ethanol was refluxed for 6 h under nitrogen. The solid formed was separated by filtration and generously washed with hot ethanol. Finally the residue was recrystallized from chloroform to produce the bimetallic complex as a yellow solid (385 mg; 0.50 mmol); yield, 67%; m.p. 270 °C (d). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 10.12 (dd, 2H, $J = 4.2$, 1.8 Hz), 8.58 (m, 4H, overlapped), 8.45 (s, 4H), 8.33 (d, 2H, $J = 8.5$ Hz), 7.81 (dd, 2H, $J = 8.1$, 4.2 Hz). IR (KBr), νCO 1984.1; 2052.9 cm^{-1}. Anal. calcd for $C_{26}H_{14}N_4O_4Cl_4Ru_2 \cdot CH_3CH_2OH$ (%): C, 40.20; H, 2.41; N, 6.69. Found (%): C, 41.09; H, 2.00; N, 7.18.

DNP[Ru(CO)$_2$Cl$_2$]$_2$

A mixture of DNP (250 mg; 0.75 mmol) and $[Ru(CO)_2Cl_2]_n$ (excess) in ethanol was refluxed for 6 h under nitrogen. The formed solid was separated by filtration and generously washed with hot ethanol. The residue was recrystallized from chloroform producing the bimetallic complex as a yellow solid (300 mg; 0.38 mmol); yield, 51%; m.p. 250 °C (d). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.14 (dd, 2H), 9.18 (d, 2H), 8.80 (d, 2H), 8.63 (m, 4H), 8.42 (m, 1H), 7.90 (dd, 2H). ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.45 (dd, 2H, $J = 1.7$, 4.2 Hz), 9.26 (d, 2H, $J = 8.2$), 9.21 (d, 2H, $J = 8.6$ Hz), 9.12 (d, 2H, $J = 8.6$ Hz), 8.85 (m, 3H, overlapped), 8.07 (dd, 2H, $J = 8.2$, 4.2 Hz). IR (KBr), νCO 2005.6; 2067.3 cm^{-1}. Anal. calcd for $C_{26}H_{14}N_4O_4Cl_4Ru_2 \cdot CH_3CH_2OH$ (%): C, 38.72; H, 2.29; N, 8.36. Found (%): C, 39.06; H, 1.86; N, 8.00.

Acknowledgements

The authors acknowledge the financial support provide by Fondecyt-Chile (project 1050168) and CEPEDEQ University of Chile. The authors would like to thank CYTED (Project V.9).

REFERENCES

1. Cole Hamilton DJ. *J. Chem. Soc., Chem. Commun.* 1980; 1213.
2. Aguirre P, Moya SA, Sariego R, Le Bozec H, Pardey A. *Appl. Organometal. Chem.* 2002; **16**: 597–600.
3. Aguirre P, López R, Villagra D, Azócar-Guzmán I, Pardey A, Moya SA. *Appl. Organometal. Chem.* 2003; **17**: 36.
4. Patent no. JP 2001006760 application JP-1999-171413.
5. Majewicz TG, Caluwe P. *J. Org. Chem.* 1979; **39**: 720.
6. Majewicz TG, Caluwe P. *J. Org. Chem.* 1975; **40**: 3407.
7. Richmond MG. *J. Organomet. Chem.* 1993; **457**: 121.
8. Kelly JM, Vos JG. *Angew. Chem., Int. Edn Engl.* 1982; **21**: 628.
9. Haasnoot JM, Hinrichs W, Vos O. *J. Inorg. Chem.* 1986; **25**: 4140.
10. Ishida H, Tanaka K, Morimoto M, Tanaka T. *Organometallics* 1986; **5**: 724.
11. Tanaka H, Nagao H, Tanaka K. *Inorg. Chem.* 1992; **31**: 1971.
12. Tanaka H, Tzeng BC, Nagao H, Peng S-H, Tanaka K. *Organometallics* 1992; **11**: 3172.
13. Tanaka H, Nagao B-C, Peng S-H, Tanaka K. *Inorg. Chem.* 1993; **32**: 1508.
14. Eskelinen E, Haukka M, Venalainen T, Pakkanen TA, Wasberg M, Chardon-Noblat S, Deronzier A. *Organometallics* 2000; **19**: 163.
15. Vlcek Jr A. *Chem. Abstr.: Inorg. Chem.* 1993; **5**: 1.
16. Lehn JM, Ziesel R. *J. Organomet. Chem.* 1990; **382**: 157.
17. Avila L, Pakkanen TA, Krause O. *J. Mol. Catal.* 1993; **84**: 145.
18. Riesgo EC, Jin X, Thummel RP. *J. Org. Chem.* 1996; **61**: 3017.
19. Ezel EL, Thummel RP, Martin GE. *J. Heterocycl. Chem.* 1984; **21**: 817.