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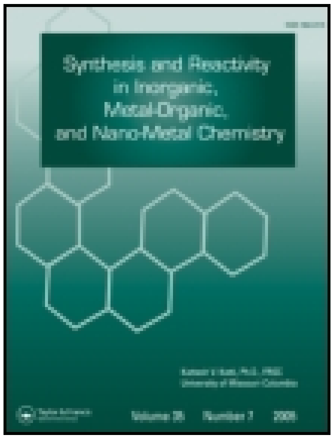

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Synthesis and Catalytic Activity of Semiconducting p-Cymene Ruthenium 1,3,4-Thiadiazole and 1,2,4-Triazole Complexes

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Synthesis and Catalytic Activity of Semiconducting *p*-Cymene Ruthenium 1,3,4-Thiadiazole and 1,2,4-Triazole Complexes

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The novel ruthenium(II) complexes containing 5-(pyridin-4-yl)-1,3,4-thiadiazol-2-amine(1) and 4-amino-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol (2) ligands were synthesized and characterized by UV-Vis, IR, NMR, and elemental analysis. The complexes have been employed as catalysts for the transfer hydrogenation of acetophenone in the presence of KOH using 2-propanol as a hydrogen source at 82°C. Moreover, the temperature dependence of conductivity of the complexes was determined in the temperature range of 303–373 K. The complex [Ru(1,2)(*p*-cymene)Cl_2] exhibits the semiconducting behavior, as the conductivity of the samples is increased with the increase in temperature.

Keywords 1, 3, 4-thiadiazole ligand, 1, 2, 4-triazole ligand, ruthenium complexes, transfer hydrogenation of ketones, organometallic semiconductor

INTRODUCTION

Electrical properties of metal complexes depend on their geometric shape, crystal structure and metal-ligand interaction.[1,2] Semiconductor properties of synthesized ruthenium complexes are investigated considering the -N, -S bonded interactions in the aromatic chain of its ligands and the metal-ligand interactions. Thus, the contribution of ruthenium complexes to the semiconductor technology is targeted. Conductivity measurements of complexes were synthesized by pellet.[3–5]

In addition to their economic importance and contribution to the quality of life, catalyst is interesting for the subtlety with which they go about their business.[6] Many studies during the last decade have been designed to identify a good Ru(II) catalyst for transfer hydrogenation of ketones.[7,8] Ruthenium(II) complexes with properties of a catalyst increases the importance of every day.[10–12] Synthesized complexes have been employed as catalysts for the TH of acetophenone derivatives.

EXPERIMENTAL

All manipulations were performed under argon using Standard Schlenk Techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under argon before use.

NMR spectra were recorded at 297 K on a Bruker 300 MHz Ultrashield TM NMR spectrometer at 300 MHz (^{1}H), 75.48 MHz (^{13}C) (Inonu University, Turkey). Organic carbon, hydrogen, nitrogen, and sulfur contents were determined using a Leco CHNS-932 analyzer (Inonu University, Turkey). Melting points were determined using an ELECTROTHERMAL 9100 melting point detection apparatus (Firat University, Turkey) and are uncorrected. Infrared spectra were measured with a Perkin-Elmer Spectrum One FTIR system and recorded using a universal ATR sampling accessory within the range 550–4000 cm^{-1} (Bingol University, Turkey). GC measurements for catalytic experiments were performed using a Younglin Acme 6100 GC instrument (Çanakkale Onsekiz Mart University, Turkey) with a HP5 cap. The dimeric complex [Ru(*p*-cymene)Cl_2]$_2$ was synthesized by the reported[13,14] method. A Shimadzu 3600 UV-VIS-NIR spectrophotometer was used to record the electronic spectra (Bingol University, Turkey). The dimeric complex [Ru(*p*-cymene)Cl_2]$_2$ was synthesized by the reported[13,14] method. The electrical resistances of the samples were measured by two probe method using a KEITHLEY 6517A electrometer (Firat University, Turkey).

Materials and Syntheses

*Synthesis of 5-(pyridin-4-yl)-1,3,4-thiadiazol-2-amine (**1**)*

L_1 was synthesized according to literature.[15] ^{1}H NMR (δ, DMSO-*d6*): 7.50 (s, 2H, NH_2), 7.68 (dd, $J = 5.23$, 1.83, 2H), Ar.C-CH, 8.70 (d, $J = 5.86$, 2H, Ar. N-CH). IR(cm^{-1}): 3220, 3170, 3110, 3000, 1621.

*Synthesis of 4-amino-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol (**2**)*

L_2 was synthesized according to literature.[16] ^{1}H NMR (δ, DMSO-*d6*): 14.02 (br, 1H, SH), 8.74 (dd, $J = 6.23$, 1.47, 2H, pyridyl H_3, H_5), 7.99 (dd, $J = 6.23$, 1.47, 2H, pyridyl H_2, H_6),

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5.84 (br, 2H, NH_2); ^{13}C NMR (d, DMSO-d6): 168.4, 150.9, 148.1, 133.6, 122. IR(cm^{-1}): 3380, 3200, 3090, 3000, 2925, 2762, 2560.

*Synthesis of [Ru(**L1**)(p-cymene)Cl$_2$](**1a**)*

Ru-*p*-cymene dimer (306 mg, 0.5 mmol) was added to a THF solution (5 mL) of **1** ligand (178 mg, 1.0 mmol). The color of mixture immediately turned from brown to yellow. The reaction mixture was stirred at room temperature for 2 h. The precipitate was filtered off, washed with THF and filtered off again, to remove un-reacted **1**. The residue was dissolved in CH_2Cl_2 (5 mL) and then precipitated with diethyl ether (10 mL) to give the dark yellow solid with. Yield: 1.95 g, 91%. mp 225°C. Anal. Calcd. for $C_{18}H_{23}N_4Cl_2SRu$ (%): C, 43.3; H, 4.6; N, 11.2; S, 6.4. Found (%): C, 41.8; H, 4.1; N, 11.4; S, 6.2. ^{1}H (δ, DMSO-*d6*): 7.60 (s, NH_2, 2H), 8.90 (d, $J = 6.3$, Ar.C-CH, 2H), 8.63 (d, $J = 5.1$, Ar. N-CH, 2H) 5.58 (d, $J = 5.9$, =CH, 2H), 5.39 (d, $J = 5.9$, =CH, 2H) 2.80–2.84 (m, CH, 1H), 2.08 (s, -CH_3, 3H) 1.75 (s, $C(CH_3)_2$, 6H). ^{13}C NMR (δ, DMSO-*d6*): 18.4, 22.0, 30.5, 86.0, 86.8, 100.6, 106.9, 120.7, 138.3, 116.0, 154.5, 170.3. IR(cm^{-1}): 1604($\nu_{C=N}$).

*Synthesis of [Ru(L$_2$)(p-cymene)Cl$_2$](**2a**)*

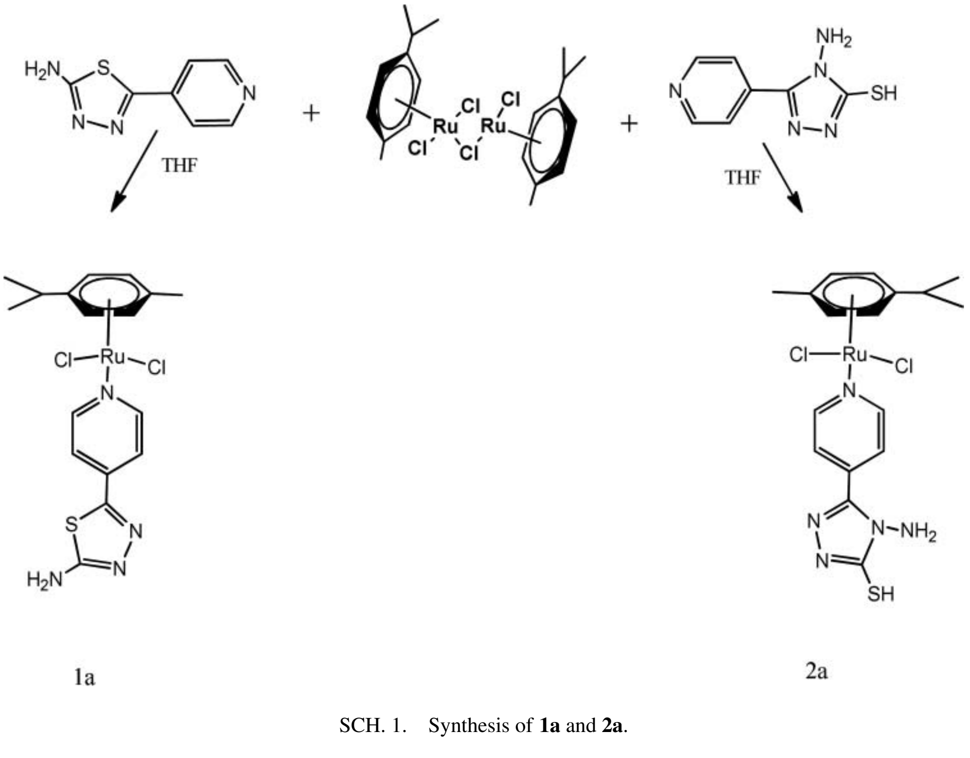
Ru-*p*-cymene dimer (306 mg, 0.5 mmol) was added to a THF solution (5 mL) of **2** ligand (193 mg, 1.0 mmol). The color of mixture immediately turned from brown to yellow. The reaction mixture was stirred at room temperature for 2 h. The precipitate was filtered off, washed with THF and filtered off again, to remove un-reacted **2**. The residue was dissolved in CH_2Cl_2 (5 mL) and then precipitated with diethyl ether (10 mL) to give the yellow solid with. Yield: 1.95 g, 91%. mp 235°C. Anal. Calcd. for $C_{18}H_{24}N_5Cl_2SRu$ (%): C, 42.0; H, 4.7; N, 13.6; S, 6.2. Found (%): C, 41.6; H, 4.2; N, 13.0; S, 6.3.^{1}H NMR (δ, DMSO-*d6*): 8.69–8.74 (m, =CH, 2H), 8.18 (d, $J = 6.6$, =CH, 1H), 7.97 (d, $J = 6.6$, =CH, 1H), 5.78 (dd, $J = 17.5, 6.6$, =CH, 2H), 5.75 (dd, $J = 17.5, 6.6$, =CH, 2H), 2.84–2.77 (m, -CH, 1H), 2.07 (s,CH_3, 3H), 1.15 (d, $J = 7.0$, CH_3, 6H). ^{13}C NMR (δ, DMSO-*d6*): 18.4, 22.0, 30.4, 86.0, 86.9, 100.6, 106.9, 120.3, 123.4, 126.6, 129.3, 151.0. IR(cm^{-1}): 1603($\nu_{C=N}$).

RESULTS AND DISCUSSION

Synthesis and Characterization of Ru^{II} Complexes

[Ru_2(*p*-cymene)$_2Cl_4$] reacts with pyridine-based ligands in (**1a, 2a**) THF at room temperature in (Scheme 1) and the resulting air-stable heteroleptic mononuclear complexes can be isolated. Synthesized complexes were soluble in most organic solvents and were fully characterized by elemental analysis and spectroscopic methods.

All complexes gave ^{1}H- and ^{13}C-NMR spectra corresponding to the proposed formulations. Despite many attempts, X–ray quality crystals of **1a** and **2a** were not obtained. Therefore, the stereochemistry of the complexes was determined on the basis of ^{1}H- and ^{13}C-NMR spectra, which exhibited the expected singlet resonances. In the ^{1}H-NMR spectra, Me-Ph-CH(Me)$_2$ protons for **1a** and **2a** were observed as a singlets at 2.09 ppm for both complexes. Me-C_6H_4-CH(Me)$_2$ protons were observed as doublet at 1.85–1.21 ppm in **1a** and as multiplets at 1.18 and 1.28 ppm in **2a** Me-C_6H_4-*CH*(Me)$_2$ protons for **1a** and **2a** were observed as multiplets at 2.81–2.86 ppm and 2.80–2.88 ppm, respectively. Me-*C_6H_4*-CH(Me)$_2$ protons for **1a** and **2a** were observed as multiplets at 5.77–5.84 ppm for both complexes.



SCH. 1. Synthesis of **1a** and **2a**.

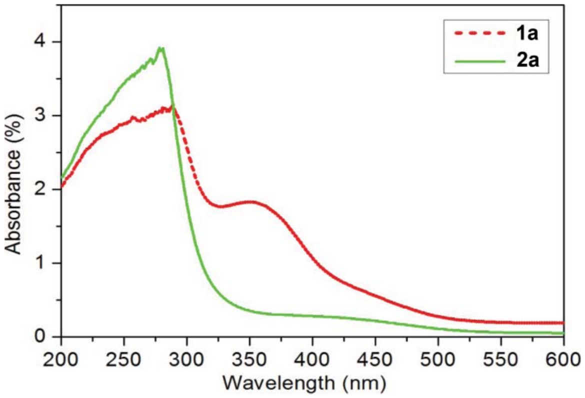


FIG. 1. The electronic absorption spectra **1a** and **2a**, recorded in 5×10^{-5} M CH_3OH (color figure available online).

Py-H_o and –H_m protons for **1a** were observed as doublets in a 2:2 ratio at 8.63 ppm and 8.90 ppm, respectively. On the other hand, Py-H_o and –H_m protons for **2a** were observed as doublets in a 2:2 ratio at around 8.74–8.69 ppm and 8.18 ppm. From ^{13}C-NMR spectra, while sp^3-hybridized carbon peaks observed as three singlets, sp^2- hybridized carbon peaks observed as nine singlets for both complexes **1a** and **2a**.

UV–Vis Spectra

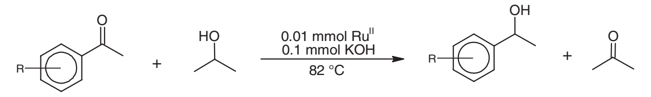
The electronic transition for all the complexes were recorded in methyl alcohol solution. The absorption spectra of complexes **1a** and **2a** mainly consist of two resolved bands in the range 200–600 nm.

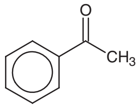
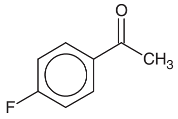
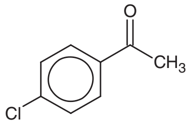
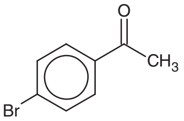
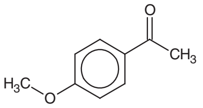
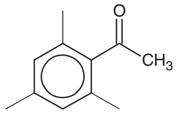
The absorption spectra of the two Ru(II) complexes are characterized by intense π - π^* ligand transitions in the UV and metal-to -ligand charge transfer (MLCT) transition in the visible region[17]. Figure 1 showed the absorption spectra of **1a** and **2a** in methyl alcohol solutions. For metal-ligand charge transfer complexes **1a** and **2a** in the range 350–500 nm and 250–300 nm transitions between the ligands is observed for the π-π^*.[18,19]

Catalytic Studies

The complexes **1a** and **2a** have been tested as catalyst in the transfer hydrogenation (TH) of ketones with KOH in 2-propanol under argon atmosphere to ascertain to most optimum conditions (Table 1). Catalytic experiments were carried out under identical conditions to allow comparison of results. Very rapid conversions are achieved at 82°C. The catalytic conversions become notably slower when the temperature is decreased. In general, although both catalysts were effective for TH of ketones, **1a** is much more active catalyst than **2a**. Ru^{II} complexes are more efficient catalyst for electron withdrawing substituent such as F-, Cl-, and Br- on the para position of the aryl ring of the acetophenone derivatives. These results are consistent with other researchers.[20,21] When the electron donating group is introduced at the aryl ring of the ketone, catalytic activity decreases. A plausible mechanism has been proposed for the previously described results (Figure 2).

TABLE 1
Catalytic activity for transfer hydrogenation of ketones catalyzed by Ru(II) complexes[a]



Entry	Substrate	Catalyst	Conversion (%)
1		**1a**	96 (26)[b]
2		**2a**	56
3		**1a**	98
4		**2a**	63
5		**1a**	95
6		**2a**	59
7		**1a**	95
8		**2a**	55
9		**1a**	78
10		**2a**	29
11		**1a**	42
12		**2a**	11

[a]Reactions were carried out at 82°C using 1 mmol substrate with 0.01 mmol Ru^{II} in 5 mL of 2-propanol for 0.5 h. [b]Reactions were carried out at 25°C using 1 mmol substrate with 0.01 mmol Ru^{II} in 5 mL of 2-propanol for 1 h.

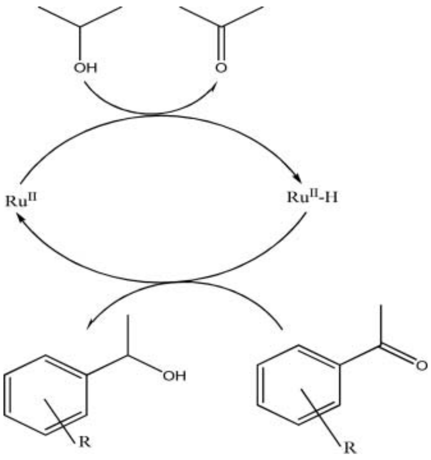


FIG. 2. Proposed mechanism for transfer hydrogenation of arylketones catalyzed Ruthenium complexes in the presence of KOH in 2-propanol.

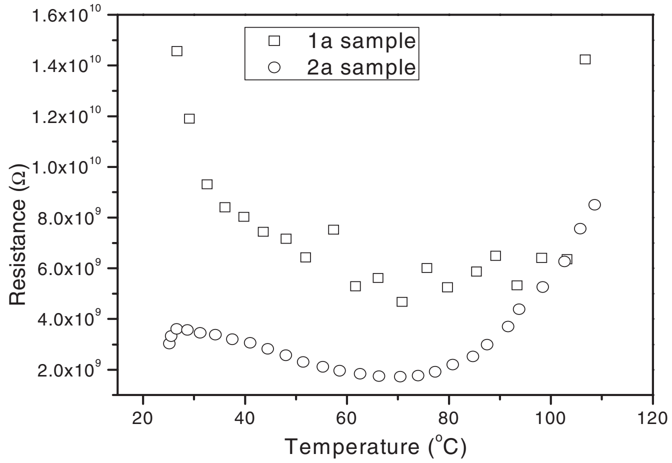


FIG. 3. Plots of electrical resistance vs. temperature of the samples.

Semiconductive Properties

Figure 3 shows the curves of electrical resistance of the samples. As seen in Figure 2, the electrical resistance of the samples is decreased up to 70°C and then is increased with temperature. The electrical conductivity of **2a** sample is higher than that of **1a** sample. The difference in electrical conductivities of the samples is resulted from the chemical structure. The obtained results indicate that the studied samples exhibit the semiconductive properties.

CONCLUSIONS

In this work, we reported the preparation and characterization of novel Ru(II) complexes (**1a** and **2a**) containing pyridine-based ligands and their catalytic activities for the hydrogen transfer reaction of acetophenone derivatives with the use of 2-propanol in the presence of KOH. Catalytic reactions show that **1a** is more efficient catalyst than **2a** for TH of simple ketones. The efficiency of the catalyst seems to depend on the ligands of complexes and the substituents of acetophenone.

The complexes [Ru(**L1–2**)(*p*-cymene)Cl_2] exhibits the conducting behavior, as the conductivity of the samples is increased with the increase in temperature. In the **2a** and **1a** study of the catalytic complex, the complex activity were found to be higher than the yield.

REFERENCES

1. Yakuphanoglu, F. Photovoltaic properties of the organic–inorganic photodiode based on polymer and fullerene blend for optical sensors. *Sens. Actuators, A* **2008**, *141*, 383–389.
2. Singh, N.; Gupta, S. Solid state electrical conductance properties of some new bimetallic salts and heterometallic coordination polymers derived from bis (1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolato) cuprate(II) ion. *Synth. Met.* **1999**, *107*, 167–174.
3. Singh, N.; Singh, V.K. Electrical properties of complex bimetallic salts $[M(N–N)_3]^{2+}[Cu(MNT)_2]^{2-}$ and heterobimetallic $Ag^I–Cu^{II}/Hg^{II}–Cu^{II}$ bis(maleonitriledithiolato) bridged coordination polymers. *Int. J. Inorg. Mater.* **2000**, *2*, 167–175.
4. Srivastava, K.P.; Srivastava, G.P.; Arya, S.K.; Madhok, K.L. Synthesis of niobium pentachloride complexes with 1,5-diaryl-substituted 2, 4-dithiobiurets and 1,5-diaryl-substituted 2-thiobiurets and their semiconducting properties *J. Chern., Eng. Data* **1980**, *25*, 173–175.
5. Yakuphanoglu, F.; Sekerci, M.; Evin, E. The determination of the conduction mechanism andoptical band gap of fluorescein sodium salt. *Phys. B* **2006**, *382*, 21–25.
6. Shriver, D.F.; Atkins, P.W. *Inorg. Chem.* **1999**, 585.
7. Dayan, O.; Cetinkaya, B. Mono- and binuclear ruthenium (II) complexes containing pyridine-2,6-diimine (Pydim) ligands: synthesis, characterization and catalytic activity in the transfer hydrogenation of acetophenone. *J. Mol. Catal. A–Chem.* **2007**, *271*, 134–141.
8. Cetin, A.; Dayan, O. Transfer hydrogenation of acetophenone catalyzed by in situ generated 2,6-bis(5-thioxo-4,5-dihydro-1,2,4-triazole-3-yl)pyridine-ruthenium(II) complexes. *Chin. J. Chem.* **2009**, *27*, 1–10.
9. Clercq, B.D.; Verpoort, F. A new class of ruthenium complexes containing Schiff base ligands as promising catalysts for atom transfer radical polymerization and ring opening metathesis polymerization. *J. Mol. Catal. A–Chem.* **2002**, *180*, 67–76.
10. Clercq, B.D.; Verpoort, F. Synthesis and evaluation of a new class of ruthenium-based catalytic systems for atom transfer radical addition and enol ester synthesis. *J. Organomet. Chem.* **2003**, *672*, 11–16.
11. Aydemir, M.; Baysal, A.; Meric, N.; Gümgüm, B. New active ruthenium(II) complexes based N3,N3′-bis(diphenylphosphino)-2,2′-bipyridine-3,3′-diamine and P,P′-diphenylphosphinous ester ligands for transfer hydrogenation of aromatic ketones by propan-2-ol acid-P,P′-[2,2′-bipyridine]-3,3′-diyl. *J. Organomet. Chem.* **2009**, *694*, 2488–2492.
12. Bennett, M.A.; Smith, A.K. Arene ruthenium(II) complexes formed by dehydrogenation of cyclohexadienes with ruthenium (III) trichloride. *J. Chem. Soc., Dalton Trans.* **1974**, 233.
13. Bennett, M.A.; Huang, T.N.; Matheson, T.W.; Smith, A.K. (η6-hexamethylbenzene) ruthenium complexes. *Inorg. Synth.* **1982**, *21*, 74.
14. Cetin, A.; Cansız, A. *Synthesis characterization of some compounds including rings of 1,3,4-oxadiazoale, 1,3,4-thiadiazole, and 1,2,4-triazol*. Fırat University Graduate School of Natural and Applied Sciences Department of Chemistry, Elazig, Turkey, **2004**.
15. Cetin, A. Accelerated synthesis of novel accelerated synthesis of novel 1,2,4-triazolo[3,4-b] [1,3,4] thiadiazepines under microwave irradiation. *Heterocyclic* **2006**, *68*, 1901–1907
16. Liu, Y.J.; Zenga, C.H.; Huang, H.L.; He, L.X.; Wu, F.H. Synthesis, DNA-binding, photocleavage cytotoxicity and antioxidant activity of ruthenium (II) polypyridyl complexes. *Eur. J. Med. Chem.* **2010**, *45*, 564–571
17. Nakajima, K.; Ishibashi, S.; Inamo, M.; Kojima, M. Thermal and photo substitution reactivity and crystal structures of tridentate Schiff base–ruthenium(II) complexes containing phosphorus or sulfur donor atoms. *Inorg. Chim Acta* **2001**, *325*, 36–44
18. Pearson, P.; Bond, A.M.; Deacon, G.B.; Forsyth, C.; Spiccia, L. Synthesis and characterisation of bis(2,2’-bipyridine)- (4-carboxy-40-(pyrid-2-ylmethylamido) 2,2’-bipyridine)-ruthenium(II) di(hexafluorophosphate): comparison of spectroelectrochemical properties with related complexes. *Inorg. Chim. Acta* **2008**, *361*, 601–612
19. Aydemir, M.; Durap, F.; Baysal, A.; Meric, N.; Buldağ, A.; Gümgüm, B.; Özkar, S.; Yıldırım, L.T. Novel neutral bis(phosphinite) bridged dinuclear ruthenium(II) arene complexes and their application in transfer hydrogenation of aromatic ketones: X-ray structure of a new Schiff base, N3,N3′-di-2-hydroxybenzylidene-[2,2’]bipyridinyl-3,3′-diamine. *J. Mol. Catal. A–Chem.* **2010**, *326*, 75–81.
20. Faller, J.W.; Lavoie, A.R. Catalysts for the asymmetric transfer-hydrogenation of ketones derived from (L)-prolinamide and $(cymeneRuCl_2)_2$ or $(Cp^*RhCl_2)_2$. *Organometallics* **2001**, *20*, 5245–5247.
21. Pelagatti, P.; Carcelli, M.; Calbiani, F.; Cassi, C.; Elviri, L.; Pelizzi, C.; Rizzotti, U.; Rogolino, D. Transfer hydrogenation of acetophenone catalyzed by half-sandwich ruthenium (II) complexes containing amino amide ligands. Detection of the catalytic intermedidates by electrospray ionization mass spectrometry. *Organometallics* **2005**, *24*, 5836–5844.