Inorganic Chemistry Communications 14 (2011) 1884–1888

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

A novel cationic dinuclear ruthenium complex: Synthesis, characterization and catalytic activity in the transfer hydrogenation of ketones

Lei Wang [a,b], Qin Yang [a], Hua Chen [a], Rui-Xiang Li [a,*]

[a] *Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, PR China*
[b] *College of Chemistry and Chemical Engineering, Xuchang University, Xuchang, Henan 461000, PR China*

ARTICLE INFO

Article history:
Received 24 June 2011
Accepted 7 September 2011
Available online 14 September 2011

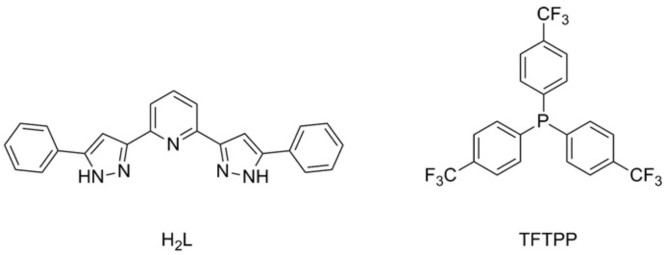
Keywords:
Ruthenium
N_4 ligand
Dinuclear complex
Transfer hydrogenation
Ketone

ABSTRACT

A novel cationic dinuclear ruthenium complex $[RuCl(HL)(TFTPP)]_2$ (H_2L = 2,6-bis(5-phenyl-1*H*-pyrazol-3-yl) pyridine; TFTPP = tri(*p*-trifluoromethylphenyl)phosphine) has been synthesized and characterized by $^{31}P\{^1H\}$ NMR, ^1H NMR, elemental analysis and X-ray crystallography. This complex is the first cationic dinuclear ruthenium complex bearing N_4 ligand characterized by single crystal X-ray analysis. It exhibits good catalytic activity for the transfer hydrogenation of ketones in refluxing 2-propanol.

Transfer hydrogenation in 2-propanol is a potentially useful protocol for the reduction of ketones to their corresponding alcohols [1-4]. It has emerged as an efficient alternative to hydrogenation of ketones for it is safe, highly selective and ecofriend [5-7]. Ru(II) complexes bearing arene are usually the most potential catalysts for transfer hydrogenation of ketones [6-20]. This kind of complexes shows the high catalytic activity and a short lifetime of active species because the arene is easily slipped from central Ru(II) in course of catalytic reaction [21]. Recently, Ru(II) complexes bearing tridentate pincer ligands have been successfully developed and explored to construct an effective catalyst system for transfer hydrogenation of ketones [22-27]. Compared with Ru(II) complexes bearing arene, Ru(II) complexes bearing tridentate pincer ligands show the long lifetime of active species due to the chelating effect of tridentate ligands for the active metal center. Especially, Ru ONO-type pincer complex shows excellent catalytic activity in transfer hydrogenations with turnover numbers up to 590,000 [28]. In the same time, some researcher's attention is focused on dinuclear ruthenium complex because of their special structures and potentially catalytic activities. Several dinuclear ruthenium complexes have been documented for transfer hydrogenation of ketones, but all of them bear arene ligands [29-31]. Therefore, to develop some new dinuclear ruthenium pincer complexes as the efficient catalysts are still strongly desired in this area. Bispyrazolyl ligands, as a kind of anionic multidentate linkers, have been successfully used to construct multinuclear transition metal complexes [32]. So we have been interested in the synthesis and application of multinuclear ruthenium complex bearing H_2L. In this paper, we synthesized and characterized a novel cationic dinuclear ruthenium complex, $[RuCl(HL)(TFTPP)]_2$ (**1**) (Structures of H_2L and TFTPP are shown in Scheme 1), and investigated its catalytic performance for the transfer hydrogenation of ketones.

Reagent-grade $RuCl_3 \cdot 3H_2O$ was used as received. Other materials TFTPP [33] and H_2L [34] were prepared with the reported methods. According to the reported result [35], $[RuCl_2(PPh_3)(Me_4BPP)]$ (Me_4BPP = 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine) could be synthesized by reacting $RuCl_3(Me_4BPP)$ with PPh_3 (1: 1) in the presence of Et_3N. Hence, we tried to synthesize complex $[RuCl_2(TFTPP)(H_2L)]$ by reacting $RuCl_3 \cdot 3H_2O$ with H_2L and TFTPP (1: 1: 1) in alcohol. Under this condition, some air-stable red crystals were isolated [36]. The single crystal of complex **1** was obtained and identified by X-ray crystallography [37]. Its crystal data and structure refinement



Scheme 1. Structures of ligands.

---

* Corresponding author: Tel./fax: +86 28 8541 2904.
E-mail address: liruixiang@scu.edu.cn (R.-X. Li).

1387-7003/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2011.09.003

results are presented in Table 1. The selected bond distances and bond angles are compiled in Table 2. Its structure is shown in Fig. 1. The single crystal structure of complex **1** is quite unusual and it exhibits a Ru(II) bimetallic species with the $(HL)^-$ ligand and chloride ligand, which acts as a bridge between the two ruthenium centers. The geometry around the two ruthenium centers can be defined as slightly distorted octahedral. Each ruthenium center is coordinated with one phosphorus atom of TFTPP, one chloride, three nitrogen atoms of $(HL)^-$, and one nitrogen atom of another $(HL)^-$. Another chloride anion, which is located in the outside of the coordination sphere, forms a hydrogen bond with H(10) in N–H bond. To the best of our knowledge, this is the first crystallographic determination of bimetallic ruthenium complex with this sort of ligand. From Table 2, we can find that the two bond distances between ruthenium and phosphine are almost the same. It is indicated that they are in the same chemical environment. Subsequently, the red crystals were identified by NMR. A singlet at 50.98 ppm in $^{31}P\{^1H\}$ NMR spectrum suggested that the chemical environment of two phosphorus atoms was equivalent, which is consisted with the results of X-ray crystallography. The protons on the pyridine ring in complex **1** appeared as multi-signal at 7.87–7.96 ppm in ^1H NMR spectrum and protons of N–H as a singlet at 14.56 ppm. The downfield shift of the N–H proton in complex **1** should be caused by the low electronic density and the electronic shielding effect due to the formation of hydrogen bond. The ratio of the protons of N–H to that of pyridine ring is 1: 3, which is also consisted with the results of X-ray crystallography. The elemental analysis results further confirmed the structure of complex **1**.

As a special dinuclear ruthenium complex, is the complex **1** an efficient catalyst for the transfer hydrogenation of ketones? So the catalytic activity of complex **1** was investigated in the optimum reaction condition (Table 3) [38]. This complex exhibited a good catalytic activity for the transfer hydrogenation of ketones (Entries 1–16). The nature and position of substituents in the aromatic ketones result in significant effects on the catalyst activity [39, 40]. Ketones with electron-withdrawing substituents can be reduced smoothly, while the introduction of electron-donating substituent in the substrate tends to decrease the reaction rate. The substituted acetophenones with methyl group are reduced more slowly than acetophenone (Entries 1, 6–8). Notably with an electron-donating methyl group in the *o*-position the reaction is accelerated, but when the *p*-position of substrate is substituted the rate is lowered (Entries 6, 8). Furthermore, the transfer hydrogenation of aromatic ketones with an electron-withdrawing group, such as chloro and bromo, led to the high conversions (up to 98%) (Entries 3–5, 9–10). Interestingly, this catalyst also shows excellent activity for the conversions of five and six membered cyclic ketones to their corresponding alcohols with 97 and 100% conversions (Entries 12–13). Furthermore, complex **1** was also an efficient catalyst for the transfer hydrogenation alkyl ketones and alpha-tetralone (Entries 14–16). With a reduced loading of catalyst (**1** of 0.05 mol%), phenylethanol of 71% was obtained with a high TON of 710 per Ru (Entry 2). This result is much higher than $[C_6H_4\text{-}1,3\text{-}(OPPh_2\{Ru(\eta^6\text{-p-cymene})Cl_2\})_2]$ (TON is 42 per Ru) [29], $[C_{10}H_6N_2\{NHPPh_2\text{-}Ru(\eta^6\text{-p-cymene})Cl_2\}_2]$ (TON is 95.2 per Ru) [30] and $[C_{10}H_6N_2\{OPPh_2\text{-}Ru(\eta^6\text{-p-cymene})Cl_2\}_2]$ (TON is 99 per Ru) [30], but slightly lower than $[C_{24}H_{16}N_4\{OPPh_2\text{-}Ru(\eta^6\text{-benzene})Cl_2\}_2]$ (TON is 969 per Ru) [31] and $[C_{24}H_{16}N_4\{OPPh_2\text{-}Ru(\eta^6\text{-cymene})Cl_2\}_2]$ (TON is 978 per Ru) [31]. To our delight, a low concentration **1** of 0.02 mol% could give cyclohexanol of 98%. The TON was high up to 2,450 per Ru (Entry 12). For the substituted acetophenones, cyclic ketones and alkyl ketones, complex **1** showed much higher TON than other active dinuclear ruthenium complex [29-31] even Ru ONO-type pincer complex [28].

Table 1
Crystal and results of structure refinement for complex **1**.

Formula	$C_{88}H_{56}Cl_2F_{18}N_{10}P_2Ru_2$
Formula weight [g/mol]	1930.41
Temperature [K]	120
Wavelength [Å]	0.71073
Crystal system, space group	Triclinic, P_{-1}
Unit cell dimensions [Å]	a = 14.36413(17) α = 68.9392(13) b = 17.8100(2) β = 74.4675(11) c = 22.5516(3) γ = 85.0345(10)
Cell volume [Å^3]	5186.96(12)
Z/calculated density [g/cm^3]	2/1.236
Absorption coefficient [mm^{-1}]	0.448
F(000)	1936
Crystal size [mm]	0.42 × 0.40 × 0.36
θ range for data collection [°]	2.98–26.37
Limiting indices	$-17 \le h \le 17$, $-22 \le k \le 22$, $-28 \le l \le 28$
Reflections collected/unique	42189/21123 [$R_{int} = 0.0489$]
Completeness to θ = 26.37°	99.6%
Absorption correction	Multi-scan
Data/restraints/parameters	21123/0/1099
Goodness-of-fit on F^2	1.118
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0612$, $wR_2 = 0.1578$
R indices (all data)	$R_1 = 0.0936$, $wR_2 = 0.1722$
Largest diff. peak and hole [e/Å]	1.261 and −0.894

Table 2
Selected bond lengths (Å) and bond angles (°) for complex **1**.

Bond lengths (Å)		Bond angles (°)	
Ru1–Cl1	2.4746(11)	Ru2–Cl1–Ru1	92.57(4)
Ru1–P2	2.2695(12)	P1–Ru2–Cl1	92.06(4)
Ru1–N5	2.237(4)	P2–Ru1–Cl1	87.82(4)
Ru1–N7	2.008(3)	N4–Ru2–N2	157.73(15)
Ru1–N8	1.980(4)	N5–Ru1–P2	175.81(10)
Ru1–N9	2.125(3)	N5–Ru1–Cl1	90.24(10)
Ru2–Cl1	2.4538(10)	N6–Ru2–Cl1	86.11(9)
Ru2–P1	2.2592(12)	N6–Ru2–P1	172.14(10)
Ru2–N2	2.096(4)	N7–Ru1–N9	155.69(14)
Ru2–N3	1.980(4)		
Ru2–N4	2.015(4)		
Ru2–N6	2.220(3)		

As to the possible mechanism for the complex **1** catalyzed transfer hydrogenation, we inferred two points for it. On the one hand, the base facilitates the formation of ruthenium alkoxide by abstracting proton of the alcohol and subsequently alkoxide undergoes β-elimination to give ruthenium hydride, which is an active species in this reaction. This is the mechanism proposed by several workers on the studies of ruthenium catalyzed transfer hydrogenation by metal hydride intermediates [41]. On the other hand, compared with the activity of previously reported dinuclear ruthenium complexes [30, 31], complex **1** showed a higher TON, but it exhibited a slower reaction rate. We suggest that the N_4 ligand could efficiently stabilize the active catalytic intermediate and extend the lifetime of active species to give high TON. Even it keeps on some activity for more than 20 h (Entry 12). The long lifetime is very rare in the transfer hydrogenation catalysts. Of course, the electronically saturated precatalyst **1** might require the dissociation of a phosphine ligand, which could be relatively strongly ligated to the ruthenium center, to show a low reaction rate.

In summary, this report describes the preparation, characterization and transfer hydrogenation activity of a novel cationic dinuclear ruthenium complex bearing N_4 ligand. The catalytic reaction results demonstrated that this complex is highly efficient in transfer hydrogenation of ketones, even with 0.02 mol% loading.

Acknowledgment

We thank the financial supports from the National Natural Science Foundation of China (Nos. 20271035 and 20371032).

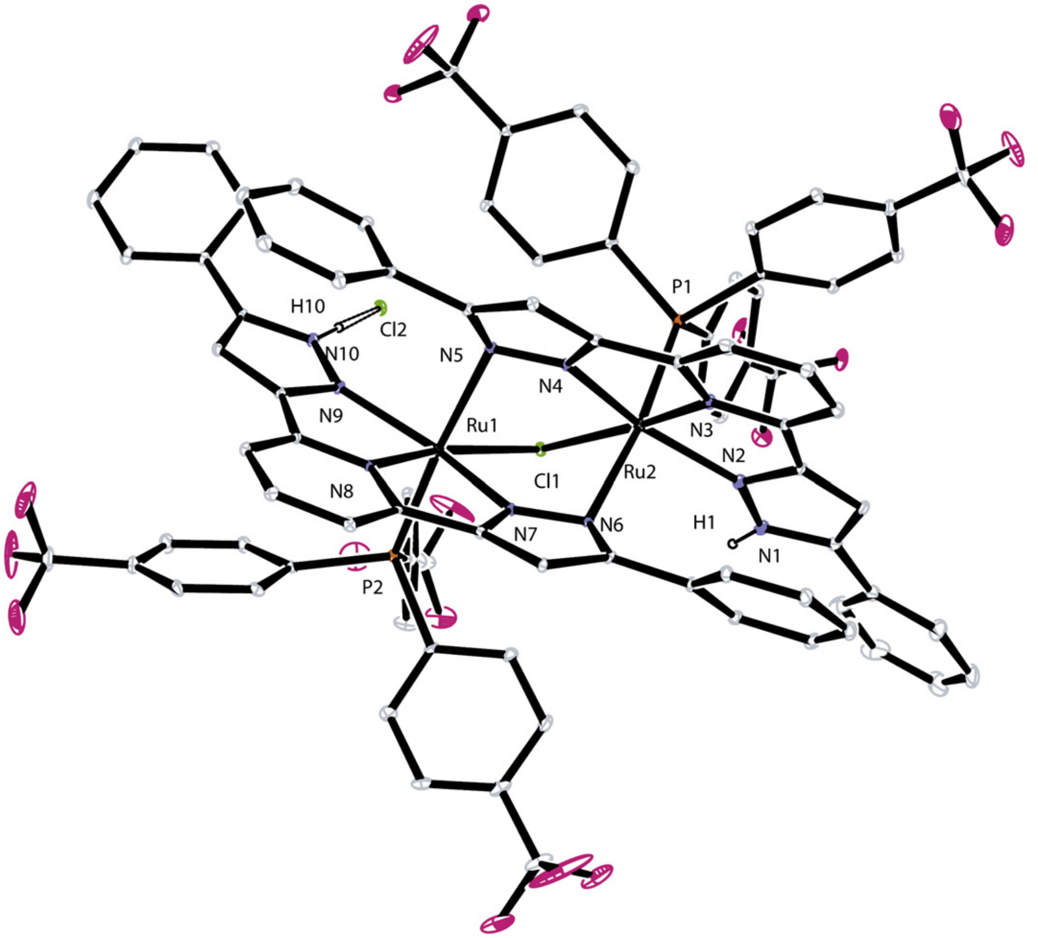


Fig. 1. ORTEP representation (ellipsoids at a 50% level) and labeling for complex **1**.

Table 3
Transfer hydrogenation of ketones with 2-propanol catalyzed by complex **1**.

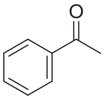
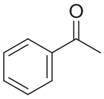
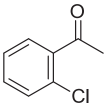
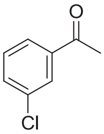
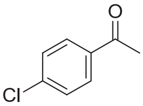
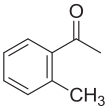
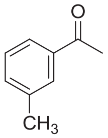
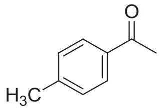
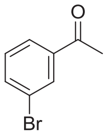
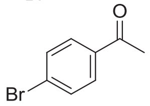
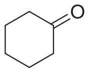
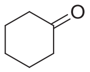
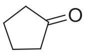
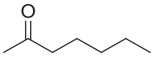
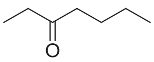
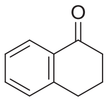
Entry	Ketone	S/[Ru]	Time (h)	Yield[a] (%)	TON
1		250	2	95	238
2		1000	7	71	710
3		250	2	98	245
4		250	2	98	245
5		250	2	96	240
6		250	3.5	92	230

Table 3 (*continued*)

Entry	Ketone	S/[Ru]	Time (h)	Yield[a] (%)	TON
7		250	3.5	92	230
8		250	3.5	88	220
9		250	2	96	240
10		250	2	95	238
11		250	2	100	250
12		2500	24	98	2450
13		250	2	97	242
14		250	2	93	232
15		250	3	90	225
16		250	2	92	230

Reaction condition: KOH/catalyst = 40/1; KOH, 0.1 mmol; catalyst, 2.5 μmol; 2-propanol, 3 mL; 82 °C.

[a] GC yield of the alcohol product.

Appendix A. Supplementary material

CCDC 822140 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.09.003.

References

[1] T. Ikariya, A.J. Blacker, Asymmetric transfer hydrogenation of ketones with bifunctional transition metal-based molecular catalysts, Accounts of Chemical Research 40 (2007) 1300–1308.

[2] X. Wu, J. Xiao, Aqueous-phase asymmetric transfer hydrogenation of ketones – a greener approach to chiral alcohols, Chemical Communications 24 (2007) 2449–2466.

[3] S. Gladiali, E. Alberico, Asymmetric transfer hydrogenation: chiral ligands and applications, Chemical Society Reviews 35 (2006) 226–236.

[4] J.S.M. Samec, J.-E. Bäckvall, P.G. Andersson, P. Brandt, Mechanistic aspects of transition metal-catalyzed hydrogen transfer reactions, Chemical Society Reviews 35 (2006) 237–248.

[5] G. Zassinovich, G. Mestroni, S. Gladiali, Asymmetric hydrogen transfer reactions promoted by homogeneous transition metal catalysts, Chemistry Review 92 (1992) 1051–1069.

[6] R. Noyori, S. Hashiguchi, Asymmetric transfer hydrogenation catalyzed by chiral ruthenium complexes, Accounts of Chemical Research 30 (1997) 97–102.

[7] M.J. Palmer, M. Wills, Asymmetric transfer hydrogenation of C=O and C=N bonds, Tetrahedron-Asymmetry 10 (1999) 2045–2061.

[8] T. Ohkuma, M. Koizumi, H. Doucer, T. Pham, M. Kozawa, K. Murata, E. Katayama, T. Yokozawa, T. Ikariya, R. Noyori, Asymmetric hydrogenation of alkenyl, cyclopropyl, and aryl ketones. rucl$_2$(xylbinap)(1,2-diamine) as a precatalyst exhibiting a wide scope, Journal of the American Chemical Society 120 (1998) 13529–13530.

[9] K. Matsumura, S. Hashiguchi, T. Ikariya, R. Noyori, Asymmetric transfer hydrogenation of α, β-acetylenic ketones, Journal of the American Chemical Society 119 (1997) 8738–8739.

[10] K.J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, The catalyst precursor, catalyst, and intermediate in the Ru^{II}-promoted asymmetric hydrogen transfer between alcohols and ketones, Angewandte Chemie (International Ed. in English) 36 (1997) 285–288.

[11] S. Hashiguchi, A. Fujii, K.J. Haack, K. Matsumura, T. Ikariya, R. Noyori, Kinetic resolution of racemic secondary alcohols by Ru^{II}-catalyzed hydrogen transfer, Angewandte Chemie (International Ed. in English) 36 (1997) 288–290.

[12] A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya, Ruthenium(II)-catalyzed asymmetric transfer hydrogenation of ketones using a formic acid-triethylamine mixture, R. Noyori, Journal of the American Chemical Society 118 (1996) 2521–2522.

[13] S. Hashiguchi, A. Fujii, J. Takehara, T. Ikariya, R. Noyori, Asymmetric transfer hydrogenation of aromatic ketones catalyzed by chiral ruthenium(II) complexes, Journal of the American Chemical Society 117 (1995) 7562–7563.

[14] V. Cadierno, P. Crochet, J. García-Alvarez, S.E. García-Garrido, J. Gimeno, Neutral and cationic (η^6-arene)-ruthenium(II) complexes containing the iminophosphorane-phosphine ligand $Ph_2PCH_2P(=N\text{-}p\text{-}C_5F_4N)Ph_2$: influence of the arene ring in

catalytic transfer hydrogenation of cyclohexanone, Journal of Organometallic Chemistry 663 (2002) 32–39.

[15] P. Crochet, M.A. Fernández-Zumel, C. Beauquis, J. Gimeno, Ruthenium(II) complexes containing 2-diphenylphosphinobenzaldehyde: synthesis and catalytic activity in transfer hydrogenation, Inorganica Chimica Acta 356 (2003) 114–120.

[16] K.Y. Ghebreyessus, J.H. Nelson, Conformationally rigid diphosphine arene-ruthenium(II) complexes as catalysts for transfer hydrogenation of ketones, Journal of Organometallic Chemistry 669 (2003) 48–56.

[17] M.L. Soriano, F.A. Jalón, B.R. Manzano, M. Maestro, Synthesis and characterization of Ru(arene) complexes of bispyrazolylazines: catalytic hydrogen transfer of ketones, Applied Organometallic Chemistry 362 (2009) 4486–4492.

[18] M. Aydemir, A. Baysal, Ruthenium-catalyzed transfer hydrogenation of aromatic ketones with aminophosphine or bis(phosphino)amine ligands derived from isopropyl substituted anilines, Polyhedron 29 (2010) 1219–1224.

[19] M.T. Reetz, X. Li, An efficient catalyst system for the asymmetric transfer hydrogenation of ketones: remarkably broad substrate scope, Journal of the American Chemical Society 128 (2006) 1044–1045.

[20] R.J. Lundgren, M.A. Rankin, R. McDonald, G. Schatte, M. Stradiotto, A formally zwitterionic ruthenium catalyst precursor for the transfer hydrogenation of ketones that does not feature an ancillary ligand N–H functionality, Angewandte Chemie (International Ed. in English) 46 (2007) 4732–4735.

[21] L. Wang, Q. Yang, H.-Y. Fu, H. Chen, M.-L. Yuan, R.-X. Li, Ru-η^6-benzene-phosphine complex-catalyzed transfer hydrogenation of ketones, Applied Organometallic Chemistry 25 (2011) 626–631.

[22] F. Zeng, Z. Yu, Construction of highly active ruthenium(II) NNN complex catalysts bearing a pyridyl-supported pyrazolyl–imidazolyl ligand for transfer hydrogenation of ketones, Organometallics 28 (2009) 1855–1862.

[23] Z.K. Yu, F.L. Zeng, X.J. Sun, H.X. Deng, J.H. Dong, J.Z. Chen, H.M. Wang, C.X. Pei, Two pseudo-N$_3$ ligands and the catalytic activity of their ruthenium(II) complexes in transfer hydrogenation and hydrogenation of ketones, Journal of Organometallic Chemistry 692 (2007) 2306–2313.

[24] H. Deng, Z. Yu, J. Dong, S. Wu, 2,6-Bis(3,5-dimethylpyrazol-1-yl)pyridine: a useful pseudo-N$_3$ ligand in efficient ruthenium(II)-catalyzed transfer hydrogenation of ketones, Organometallics 24 (2005) 4110–4112.

[25] F. Zeng, Z. Yu, Ruthenium(II) complexes bearing a pyridyl-supported pyrazolyl-n-heterocyclic carbene (NNC) ligand and their catalytic activity in the transfer hydrogenation of ketones, Organometallics 27 (2008) 6025–6028.

[26] M. Zhao, Z. Yu, S. Yan, Y. Li, Ruthenium(II) complex catalysts bearing a pyridyl-supported pyrazolyl-imine ligand for transfer hydrogenation of ketones, Journal of Organometallic Chemistry 694 (2009) 3068–3075.

[27] F. Zeng, Z. Yu, Exceptionally efficient unsymmetrical ruthenium(II) NNN complex catalysts bearing a pyridyl-based pyrazolyl-imidazolyl ligand for transfer hydrogenation of ketones, Organometallics 27 (2008) 2898–2901.

[28] Y. Zhang, X.W. Li, S.H. Hong, Ruthenium ONO-type pincer complex: synthesis, structural characterization, and catalysis, Advanced Synthesis and Catalysis 352 (2010) 1779–1783.

[29] R. Cerón-Camacho, V. Gómez-Benítez, R.L. Lagadec, D. Morales-Morales, R.A. Toscano, Ketone transfer hydrogenation reactions catalyzed by a phosphinite ruthenium PCP complex: The X-ray crystal structure of [C_6H_4-1,3-($OPPh_2${Ru(η^6-*p*-cymene)Cl_2})$_2$], Journal of Molecular Catalysis A: Chemical 247 (2006) 124–129.

[30] M. Aydemir, A. Baysal, N. Meric, B. Gümgüm, New active ruthenium(II) complexes based N3, N3′-bis(diphenylphosphino)-2,2′-bipyridine-3,3′-diamine and P, P′-diphenylphosphinous acid-P, P′-[2,2′-bipyridine]-3,3′-diyl ester ligands for transfer hydrogenation of aromatic ketones by propan-2-ol, Journal of Organometallic Chemistry 694 (2009) 2488–2492.

[31] M. Aydemir, F. Durap, A. Baysal, N. Meric, A. Buldag, B. Gümgüm, S. Özkar, L.T. Yıldırım, Novel neutral phosphinite bridged dinuclear ruthenium(II) arene complexes and their catalytic use 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, Journal of Molecular Catalysis A: Chemical 326 (2010) 75–81.

[32] Y. Zhou, W. Chen, D. Wang, Mononuclear, dinuclear, hexanuclear, and one-dimensional polymeric silver complexes having ligand-supported and unsupported argentophilic interactions stabilized by pincer-like 2,6-bis(5-pyrazolyl) pyridine ligands, Dalton Transactions 11 (2008) 1444–1453.

[33] K.C. Eapen, C. Tamborski, The synthesis of tris-(trifluoromethylphenyl)phosphines and phosphine oxides, Journal of Fluorine Chemistry 15 (1980) 239–243.

[34] Y.M. Lou, L.X. Xiao, Z. Chen, W. Huang, X.C. Tang, Syntheses, spectral properties of novel pyridine-2,6-dicarboxylic acid derivatives and their Tb(III) complexes, Huaxue Yanjiu Yu Yingyong 20 (2008) 299–303.

[35] N.J. Beach, G.J. Spivak, Ruthenium complexes supported by 2,6-bis(pyrazol-1-yl) pyridines, Inorganica Chimica Acta 343 (2003) 244–252.

[36] General procedure for synthesis of complexs **1**: Under nitrogen atmosphere, a mixture of $RuCl_3 \cdot 3H_2O$ (0.136 g, 0.5 mmol) and H_2L (0.284 g, 0.55 mmol) was refluxed in EtOH for 5 h. The color of solution changed from black brown to deep blue slowly and further generated the blue-black precipitate. After cooled to room temperature, the precipitate was filtered, washed with EtOH and Et_2O, and dried under vacuum. Without purification, this compound was used in the following synthesis. An EtOH (10 mL) slurry of blue-black precipitate and TFTPP (0.257 g, 0.55 mmol) was treated with excess Et_3N (1 mL). The solid substance slowly dissolved and the color of solution changed to red-orange. After refluxed for 6 h, the red-orange solution was cooled to room temperature and solvent was removed under vacuum to give red solid substance. The solid was extracted with Et_2O (25 mL) and filtered through Celite. The volume of the filtrate was reduced to approximately 10 mL under vacuum and n-hexane of 30 mL was carefully layered and allowed to slowly diffuse into the Et_2O solution. Over 24 h, some red crystals were obtained. The crystals were filtered and dried under vacuum. **1**: Yield (0.405 g, 60%). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ (ppm) 50.98 (s). ^1H NMR (400.1 MHz, DMSO-d_6): δ (ppm) 6.30-7.67 (m, 48H); 7.87-7.96 (m, 6H); 14.56 (s, 2H). Anal. Calc. for $C_{88}H_{56}Cl_2F_{18}N_{10}P_2Ru_2$ (%): C, 54.75; H, 2.92; N, 7.26. Found (%): C, 54.53; H, 3.05; N, 7.15.

[37] A single crystal that was suitable for the X-ray crystallographic analysis was obtained by diffusing n-hexane into the Et_2O solution of complex **1**. Single crystal X-ray diffraction studies for complex **1** were carried out on a Xcalibur E diffractometer at 120 K with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). CrysAlisPro was used to treat the crystal data. Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. The structure solution and refinement were performed with the SHELXL-97 package.

[38] General procedure for transfer hydrogenation reaction: Under nitrogen atmosphere, the mixture of ketone (1.25 mmol), catalyst (2.5 μmol) and 2-propanol (2 mL) were introduced into a Schlenk tube. The solution was stirred at 82 ^{0}C for 30 min. Then 0.1 M KOH (0.1 mmol) 2-propanol solution of 1 mL was introduced to initiate the transfer hydrogenation. The reaction process was monitored by GC analysis. The hydrogenation products were analyzed by GC Agilent 6890 N equipped with FID detector and EC-WAX capillary column (30 m × 0.25 mm, 0.25 μm film). The conversions are determined by average of two runs of each catalytic reaction.

[39] J.-X. Gao, T. Ikariya, R. Noyori, A ruthenium(II) complex with a c_2-symmetric diphosphine/diamine tetradentate ligand for asymmetric transfer hydrogenation of aromatic ketones, Organometallics 15 (1996) 1087–1089.

[40] I. Özdemir, S. Yaşar, B. Çetinkaya, Ruthenium(II) N-heterocyclic carbene complexes in the transfer hydrogenation of ketones, Transition Metal Chemistry 30 (2005) 831–835.

[41] Jan-E. Backvall, Transition metal hydrides as active intermediates in hydrogen transfer reactions, Journal of Organometallic Chemistry 652 (2002) 105–111.