Polyhedron 81 (2014) 245–255

Contents lists available at ScienceDirect

Polyhedron

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

Ionic liquid based Ru(II)–phosphinite compounds and their catalytic use in transfer hydrogenation: X-ray structure of an ionic compound 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol

Murat Aydemir [a,b,*], Khadichakhan Rafikova [c], Nurzhamal Kystaubayeva [c], Salih Paşa [d], Nermin Meriç [a], Yusuf Selim Ocak [b,d], Alexey Zazybin [c], Hamdi Temel [b,e], Nevin Gürbüz [f], Ismail Özdemir [f]

[a] Department of Science, Faculty of Science, University of Dicle, 21280 Diyarbakir, Turkey
[b] Science and Technology Application and Research Center (DUBTAM), Dicle University, Diyarbakir 21280, Turkey
[c] Department of Chemical Engineering, Kazakh-British Technical University, 050000 Almaty, Kazakhstan
[d] Department of Chemistry, Faculty of Education, University of Dicle, 21280 Diyarbakir, Turkey
[e] Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Dicle University, Diyarbakir 21280, Turkey
[f] Department of Chemistry, Faculty of Science and Art, University of İnönü, 44280 Malatya, Turkey

ARTICLE INFO

Article history:
Received 29 April 2014
Accepted 27 May 2014
Available online 12 June 2014

Keywords:
Ionic compound
Phosphinite
Transfer hydrogenation
X-ray
Ruthenium

ABSTRACT

The compound 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride (**1**) was prepared from the reaction of 1-methylimidazole with epichlorohydrine. The corresponding phosphinite ligands were synthesized by the reaction 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride, $[C_7H_{15}N_2OCl]Cl$ with one equivalent of chlorodiphenylphosphine or chlorodicyclohexylphosphine, in anhydrous CH_2Cl_2 and under an inert argon atmosphere. $[Ru(\eta^6\text{-arene})(\mu\text{-}Cl)Cl]_2$ dimers readily react with the phosphinite ligands $[(Ph_2PO)\text{–}C_7H_{14}N_2Cl]Cl$ (**2**) or $[(Cy_2PO)\text{–}C_7H_{14}N_2Cl]Cl$ (**3**) at room temperature to afford the cationic derivatives $[Ru((Ph_2PO)\text{–}C_7H_{14}N_2Cl)(\eta^6\text{-}arene)Cl_2]Cl$ and $[Ru((Cy_2PO)\text{–}C_7H_{14}N_2Cl)(\eta^6\text{-}arene)Cl_2]Cl$ {*arene*: benzene (**4**), (**5**); *p*-cymene (**6**), (**7**)}. The structures of these ligands and their corresponding complexes have been elucidated by a combination of multinuclear NMR and IR spectroscopy, TGA/DTA and elemental analysis. The molecular structure of the ionic compound **1** was also determined by an X-ray single crystal diffraction study. Furthermore, the catalytic activity of complexes **4**–**7** for the transfer hydrogenation of various ketones was investigated and these complexes were found to be efficient catalysts in the transfer hydrogenation of various ketones, with excellent conversions up to 99%. Specifically, $[Ru((Cy_2PO)\text{–}C_7H_{14}N_2Cl)(\eta^6\text{-benzene})Cl_2]Cl$ (**5**) and $[Ru((Cy_2PO)\text{–}C_7H_{14}N_2Cl)(\eta^6\text{-}p\text{-cymene})Cl_2]Cl$ (**7**) act as excellent catalysts, giving the corresponding alcohols in 98–99% conversions in 5 min (TOF $\leqslant$ 1188 h^{-1}).

1. Introduction

Ionic liquids (ILs) are potential replacements for organic solvents both on laboratory and industrial scales due to their green characteristics, such as thermal stability, lack of vapor pressure, non-flammability, wide liquid range, wide range of solubility and miscibility [1–7]. They can be readily recycled, have a profound effect on the activity and selectivity of reactions and in some cases, facilitate the isolation of products. Therefore, ionic liquids are considered viable substitutes for volatile organic solvents [8]. An unusual feature of ionic liquids is the tunability of their chemical and physical properties by selection of appropriate anion-cation combinations [9]. Metal-containing ionic liquids are regarded as promising new materials that combine the properties of ionic liquids with additional intrinsic magnetic, spectroscopic or catalytic properties, depending on the incorporated metal ion [10]. ILs that contain palladium, ruthenium, platinum, gold and aluminum (and also iron, nickel, zinc and copper) have been used with success in catalysis [11,12]. Some metal (Pd, Ru, Rh, V) complex catalysts with imidazolium tags [13–16] are also termed as IL supported catalysts.

The chemistry of P-based ligands has also been intensively explored in recent years [17,18]. Many improved phosphine ligands and a variety of aminophosphine–phosphinite ligands have important applications in organometallic chemistry and catalysis, giving selective catalysts for hydroformylation, hydrosilylation

* Corresponding author. Address: Department of Chemistry, Dicle University, TR-21280 Diyarbakır, Turkey. Tel.: +90 412 248 8550x3028; fax: +90 412 248 8300.
E-mail address: aydemir@dicle.edu.tr (M. Aydemir).

http://dx.doi.org/10.1016/j.poly.2014.05.079
0277-5387/

and transfer hydrogenation [19–21]. While much energy has been devoted to the synthesis of aminophosphines and their metal complexes, similar studies on the analogous phosphinites are less extensive [22], even though some of their complexes have proved to be efficient catalysts [23,24]. Though phosphine ligands have found well-known applications in transition metal catalyzed transformations [25,26], phosphinites afford different chemical, electronic and structural properties compared to phosphines. The metal–phosphorus bond is often stronger for phosphinites compared to the related phosphine due to the presence of the electron-withdrawing P-OR group. In addition, the empty σ^*-orbital of the phosphinite $P(OR)R_2$ is stabilized, making the phosphinite a better acceptor [27].

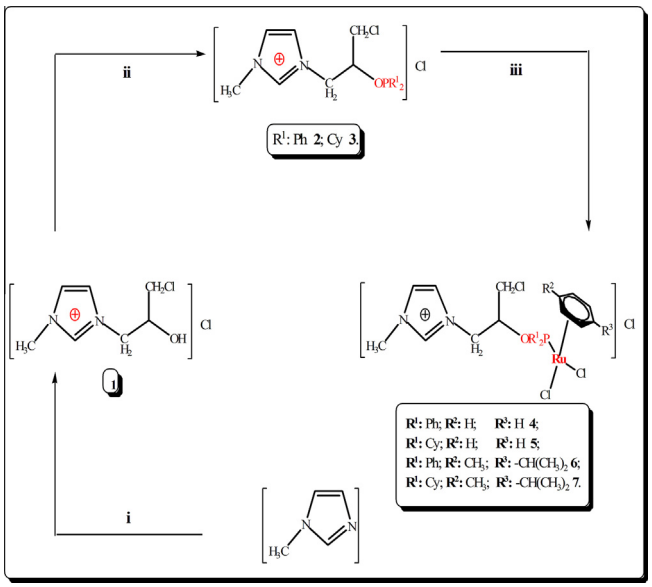
Catalytic transfer hydrogenation with the aid of a stable hydrogen donor is a useful alternative method for catalytic hydrogenation by molecular hydrogen for the reduction of ketones [28,29]. In transfer hydrogenation, organic molecules, such as secondary alcohols [30] or formic acid and its salts [31], have been employed as the hydrogen source. The use of a hydrogen donor has some advantages over the use of molecular hydrogen since it avoids the risks and constraints associated with hydrogen gas as well as the necessity for pressure vessels and other equipments. A variety of transition metal complexes are known to catalyse hydrogen transfer from an alcohol to a ketone [32]. Especially, over the last three decades, most effort on hydrogenation has been focused on the use of ruthenium catalysts. Transfer hydrogenation is usually mediated by a complex bearing rhodium, ruthenium or iridium, among which our focus has been ruthenium, because the ruthenium catalysts have excellent performances [33,34]. Furthermore, ruthenium has a cost advantage relative to other hydrogenation metals such as rhodium and iridium [35,36].

Although a lot of phosphinite ligands and their derivatives have been employed successfully as ligands in Ru(II)-promoted transfer hydrogenation of ketones [37–39] and references therein], a screening of the catalytic activities of ionic liquid based phosphinites in this reaction has not been reported as yet. To the best of our knowledge, there is no report on the utility of these complexes including phosphinite ligands based on ionic liquids in Ru(II) catalyzed transfer hydrogenation reactions. As a part of our interest in the modular design of new ligand systems with different spacers to control the electronic attributes at the phosphorus centers and to investigate their coordination chemistry, in this paper, we report (*i*) the ready synthesis of a novel ionic liquid compound, 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride, and its corresponding phosphinite ligands, (*ii*) the synthesis and full characterization of four half-sandwiches Ru(II)-arene complexes, and (*iii*) for the first time their subsequent application in transfer hydrogenation of various ketones.

2. Results and discussion

2.1. Synthesis of the compounds

The reaction of 1-methylimidazole and epichlorohydrin in ethanol at room temperature yields the compound 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride, $[C_7H_{15}N_2OCl]Cl$ (**1**) (Scheme 1), which was characterized by elemental analysis, IR, TGA-DTA and multinuclear NMR spectroscopies. The ^1H and ^{13}C NMR spectral data of **1** are consistent with the proposed structure. The ^1H NMR spectrum of 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride exhibits a characteristic signal at δ 9.26 ppm for the –(CH_3)NC*H*N–, group and two resonances at δ 7.76. and 7.78 ppm for the –NC*HCH*N– protons, which are highly deshielded. The IR spectrum also shows a broad absorption band at 3357 cm^{-1} for the O–H stretching, which is broadened and shifted



Scheme 1. Synthesis of the compounds $[C_7H_{15}N_2OCl]Cl$ (**1**), $[(Ph_2PO)–C_7H_{14}N_2Cl]Cl$ (**2**), $[(Cy_2PO)–C_7H_{14}N_2Cl]Cl$ (**3**), $[Ru((Ph_2PO)–C_7H_{14}N_2Cl)(\eta^6\text{-benzene})Cl_2]Cl$ (**4**), $[Ru((Cy_2PO)–C_7H_{14}N_2Cl)(\eta^6\text{-benzene})Cl_2]Cl$ (**5**), $[Ru((Ph_2PO)–C_7H_{14}N_2Cl)(\eta^6\text{-}p\text{-cymene})Cl_2]Cl$ (**6**) and $[Ru((Cy_2PO)–C_7H_{14}N_2Cl)(\eta^6\text{-}p\text{-cymene})Cl_2]Cl$ (**7**). (i) HCl, epichlorohydrin, EtOH; (ii) 1 equiv. Ph_2PCl or Cy_2PCl, 1 equiv. *n*-BuLi, CH_2Cl_2; (iii) ½ equiv. $[Ru(\eta^6\text{-p-cymene})(\mu\text{-Cl})Cl]_2$ or ½ equiv. $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$, CH_2Cl_2.

toward lower frequency (for details see Section 3). The structure of **1** was further confirmed by microanalysis, the results of which were found to be in good agreement with the theoretical values.

Furthermore, the structure of **1** was elucidated by X-ray crystallography, as follows. The colorless crystal of $[C_7H_{15}N_2OCl]Cl$ crystallized in the monoclinic space group of *P*2(1). The unit cell dimensions are $a = 4.90220$ Å, $b = 14.1086$ Å, $c = 7.29760$ Å. Its asymmetric unit contains two molecules and has two-fold crystallographic symmetry that can be expressed as a 2-fold screw axis with direction [0,1,0] at 0,*y*,0 with screw component [0,1/2,0]. Fig. 1 shows the asymmetric unit, which contains

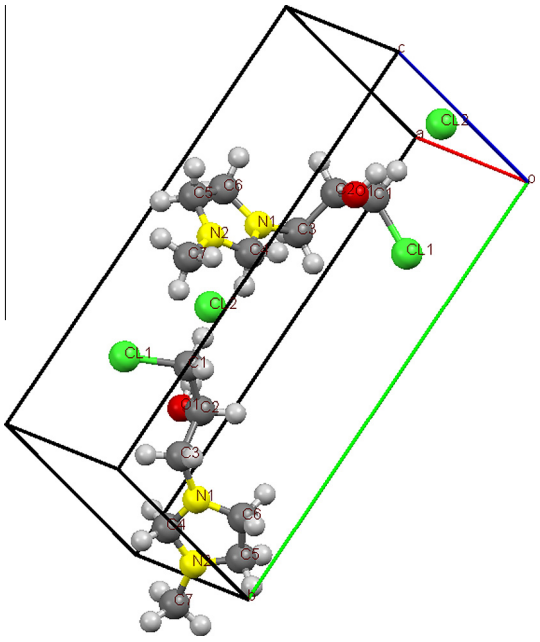


Fig. 1. The unit cell structure of 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride $[C_7H_{15}N_2OCl]Cl$ (**1**).

the 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride ligand (**1**). The distance between the stereocenters of C(2)–C′(2) in the packing structure is about 7.084 Å and some of selected bond lengths are C(2)–C(3) 1.509 Å, C(3)–N(1) 1.462 Å, C(1)–Cl(1) 1.793 Å, N(2)–C(7) 1.459 Å and C(2)–O(1) 1.414 Å. The ionic chloride, which proves the ionic liquid structure of the compound, is approximately 3.688 Å to the stereogenic C(2) atom. The structure also has an intramolecular O(1)–H(1)···Cl(2) hydrogen bond with bond distances of 0.82 and 3.075 Å and a bond angle of 166.93°. The short contacts of the atoms, the intramolecular hydrogen bonding interactions and the distances are calculated via MERCURY 3.0 and are shown in Fig. 2. Comprehensive crystal data for the structure of **1** are given in Table 1 and the selected bond angles are summarized in Table 2.

As a part of our ongoing research program for developing highly active catalysts, we synthesized two novel ionic liquid based phosphinite monodendate ligands. These phosphinite ligands, [(Ph_2PO)–$C_7H_{14}N_2Cl$]Cl (**2**) and [(Cy_2PO)–$C_7H_{14}N_2Cl$]Cl (**3**) were synthesized from the starting materials PPh_2Cl and PCy_2Cl, respectively, in CH_2Cl_2 solution by the hydrolysis method [40,41]. The LiCl salt was separated by filtration and the ligands were obtained by extracting the solvent in vacuo in good yields. The progress of this reaction was conveniently followed by $^{31}P–\{^1H\}$ NMR spectroscopy. The signals of the starting materials, PPh_2Cl at δ 81.0 ppm and PCy_2Cl at δ 127.32 ppm, disappeared and new singlets appeared downfield due to the phosphinite ligands. The $^{31}P–\{^1H\}$ NMR spectra of the phosphinites, [(Ph_2PO)–$C_7H_{14}N_2Cl$]Cl (**2**) and [(Cy_2PO)–$C_7H_{14}N_2Cl$]Cl (**3**) show single resonances at δ 118.46 and 148.76, respectively, (Fig. 3) [42–46] in line with the values previously observed for similar compounds [47–50]. A solution of [(Ph_2PO)–$C_7H_{14}N_2Cl$]Cl (**2**) in $CDCl_3$, prepared under aerobic conditions, is stable for up to 18 h and then decomposes very gradually to give the oxide and hydrolysis product diphenylphosphinous acid, $Ph_2P(O)H$ [51]. Furthermore, the $^{31}P–\{^1H\}$ NMR spectrum also displays the formation of PPh_2PPh_2 and $P(O)Ph_2PPh_2$, as indicated by signals at about δ −15.2 ppm as a singlet and δ 35.6 ppm and δ −21.4 ppm as doublets with $^1J_{(PP)}$ 226 Hz after 48 h [52]. On the contrary, a solution of [(Cy_2PO)–$C_7H_{14}N_2Cl$]Cl (**3**) is unstable under aerobic conditions and undergoes

Table 1
Crystallographic data and structure refinement for [$C_7H_{15}N_2OCl$]Cl (**1**).

Parameter	
Empirical formula	$C_7H_{15}Cl_2N_2O$
M	213.10
Crystal system	monoclinic
Space group	$P2(1)$
a (Å)	4.90220(5)
b (Å)	14.1086(5)
c (Å)	7.29760(5)
α (°)	90.00
β (°)	95.5720(5)
γ (°)	90.00
V (Å^3)	502.340(14)
Z	2
D_{calc} (g cm^{-3})	1.409
Absorption coefficient (Mo Kα) (mm^{-1})	0.604
Crystal size (mm)	0.50 × 0.25 × 0.16
Theta range for data collection (°)	2.80–33.46
Index ranges	$-7 \leqslant h \leqslant 7$, $-15 \leqslant k \leqslant 21$, $-11 \leqslant l \leqslant 11$
Reflections collected	4919
Unique reflections (R_{int})	3078 (0.0144)
Completeness of theta = 25.50°	99.5%
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	1831/26/109
Goodness of fit (GOF) on F^2	1.1040
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0397, wR_2 = 0.1556 $I > 2\sigma(I)$
R indices	R_1 = 0.0407, wR_2 = 0.1559
Largest difference in peak and hole (e Å^{-3})	0.554 and −0.250

Additional material available from Cambridge Crystallographic Data Center as deposition No: CCDC 986387 comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

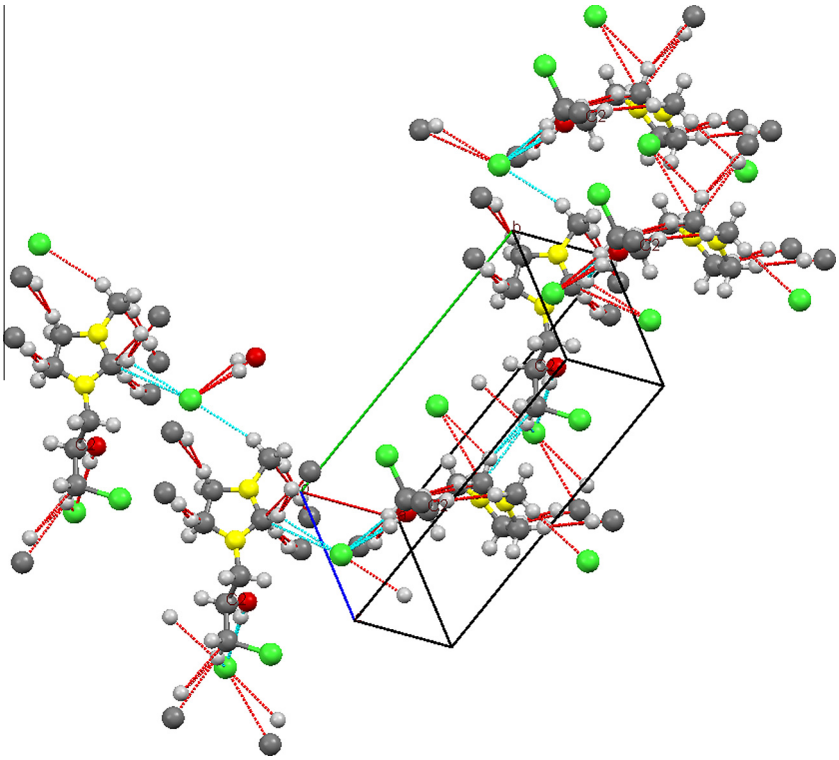


Fig. 2. The packing structure and short contacts of 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride [$C_7H_{15}N_2OCl$]Cl (**1**).

Table 2
Selected bond angles (°) of compound $[C_7H_{15}N_2OCl]Cl$ (**1**).

Atoms	Angle	s.u.	Atoms	Angle	s.u.
H1–O1–C2	109.46	0.14	N2–C5–H5A	110.36	0.16
C3–N1–C4	124.49	0.12	N2–C5–H5B	110.36	0.17
C3–N1–C6	126.41	0.12	N2–C5–C6	106.80	0.17
C4–N1–C6	109.08	0.13	H5A–C5–H5B	108.59	0.19
C4–N2–C5	109.07	0.13	H5A–C5–C6	110.36	0.18
C4–N2–C7	125.72	0.15	H5B–C5–C6	110.36	0.16
C5–N2–C7	125.21	0.17	Cl1–C1–C2	112.25	0.11
O1–C2–H2	108.02	0.13	Cl1–C1–H1A	109.15	0.14
O1–C2–C3	108.12	0.12	Cl1–C1–H1B	109.16	0.13
O1–C2–C1	112.92	0.13	C2–C1–H1A	109.15	0.16
H2–C2–C3	108.02	0.14	C2–C1–H1B	109.15	0.15
H2–C2–C1	108.02	0.13	H1A–C1–H1B	107.87	0.17
C3–C2–C1	111.57	0.13	N1–C6–C5	106.82	0.14
N1–C3–C2	111.23	0.13	N1–C6–H6A	110.36	0.16
N1–C3–H3A	109.39	0.13	N1–C6–H6B	110.36	0.15
N1–C3–H3B	109.39	0.13	C5–C6–H6A	110.36	0.20
C2–C3–H3A	109.39	0.14	C5–C6–H6B	110.36	0.16
C2–C3–H3B	109.39	0.14	H6A–C6–H6B	108.59	0.18
H3A–C3–H3B	108.01	0.16	N2–C7–H7A	109.47	0.20
N1–C4–N2	108.22	0.13	N2–C7–H7B	109.47	0.21
N1–C4–H4A	110.06	0.14	N2–C7–H7C	109.47	0.23
N1–C4–H4B	110.06	0.13	H7A–C7–H7B	109.48	0.24
N2–C4–H4A	110.05	0.14	H7A–C7–H7C	109.48	0.23
N2–C4–H4B	110.06	0.14	H7B–C7–H7C	109.47	0.25
H4A–C4–H4B	108.40	0.14			

[i: $-x,y,½-z$].

fast decomposition. Because compound **3** is not stable enough in solution, the corresponding ruthenium(II) complexes were synthesized *in-situ*. The appropriate assignment of the ^{1}H chemical shifts was derived from 2D HH-COSY spectra and that of the ^{13}C chemical ones from DEPT and 2D HMQC spectra. The structures for these ionic based monodendate phosphinite ligands are consistent with the data obtained from ^{1}H and ^{13}C NMR, IR spectra and elemental analyses (for details see Section 3).

Reactions of the ionic based monodendate phosphinites with the metal precursors $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ and $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ are also depicted in Scheme 1. The ability of the $\{[Ru(arene)(\mu\text{-Cl})Cl]_2\}$ dimers to form mononuclear complexes of the general formula $[Ru(\eta^6\text{-}arene)Cl_2L]$ is well-known [53]. As expected, the reaction of **2** and **3** with $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ or $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ gave corresponding complexes $[Ru((Ph_2PO)\text{–}C_7H_{14}N_2Cl)(\eta^6\text{-}arene)Cl_2]Cl$ and $[Ru((Cy_2PO)\text{–}C_7H_{14}N_2Cl)(\eta^6\text{-}arene)Cl_2]Cl$ {*arene*: benzene (**4**), (**5**); *p*-cymene (**6**), (**7**)}, respectively, in high yields as air stable, red microcrystalline powders (Scheme 1). The phosphinite ligands were expected to cleave the $[Ru(benzene)Cl_2]_2$ and $[Ru(p\text{-cymene})Cl_2]_2$ dimers to give the corresponding complexes via monohapto coordination. The initial color change, i.e. from clear orange to deep red, is attributed to the dimer cleavage, most probably by the phosphinite ligand [54]. The chemical purity of the complexes was confirmed by single ^{31}P–{^{1}H} NMR signals at δ 127.82, 157.21, 124.23 and 154.25, respectively ($CDCl_3$) (Fig. 4). These complexes are highly soluble in CH_2Cl_2 and slightly soluble in hexane, so they can be crystallized from a CH_2Cl_2/hexane solution. The ^{1}H NMR spectra of complexes **4** and **5** display the (–(CH_3)-NC*H*N–) resonances as broad signals at δ 8.95 and 9.02 ppm and the C_6H_6 protons as singlets at δ 5.55 and 5.96 ppm, respectively. In the ^{13}C NMR spectra of **4** and **5**, the (–(CH_3)NCHN–) carbon signals were observed at δ 137. 10 and 137.59 ppm and the C_6H_6 carbon resonances were seen at δ 88.10 (s) and 88.11 (s) ppm, respectively. Furthermore, in the ^{13}C–{^{1}H} NMR spectra of these complexes, $J(^{31}P\text{–}^{13}C)$ coupling constants of the carbons of the phenyl rings were observed, which is consistent with the literature values [55]. The structures of the complexes were further confirmed by IR spectroscopy and microanalysis, and were found to be in good agreement with the theoretical values. Other pertinent spectroscopic and analytic data are given in Section 3.

The starting complex $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ was prepared by the reaction of the commercially available α-phellandrene (5-isopropyl-2-methylcyclohexa-1,3-diene) with $RuCl_3$ [56]. The reactions of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ with ligands **2** and **3** are depicted in Scheme 1. The reactions of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ with two equivalents of **2** and **3** in CH_2Cl_2 at room temperature gave

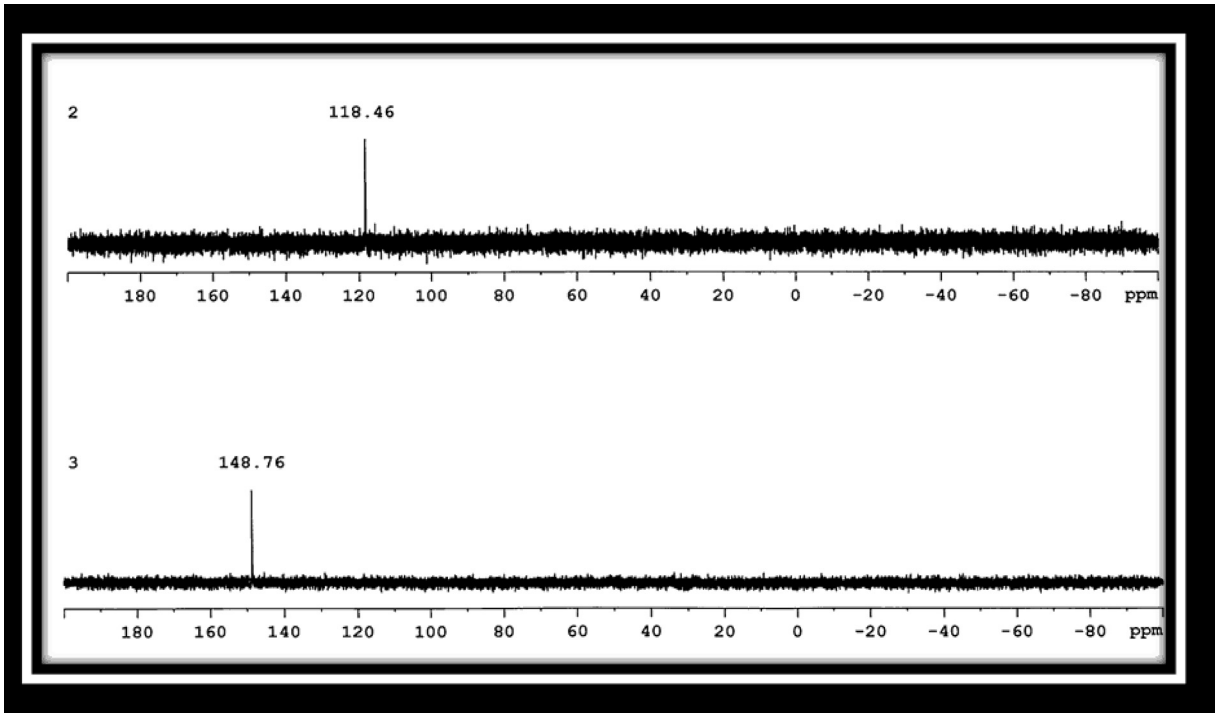


Fig. 3. The ^{31}P–{^{1}H} NMR spectra of the ligands $[(Ph_2PO)\text{–}C_7H_{14}N_2Cl]Cl$ (**2**) and $[(Cy_2PO)\text{–}C_7H_{14}N_2Cl]Cl$ (**3**) ($CDCl_3$).

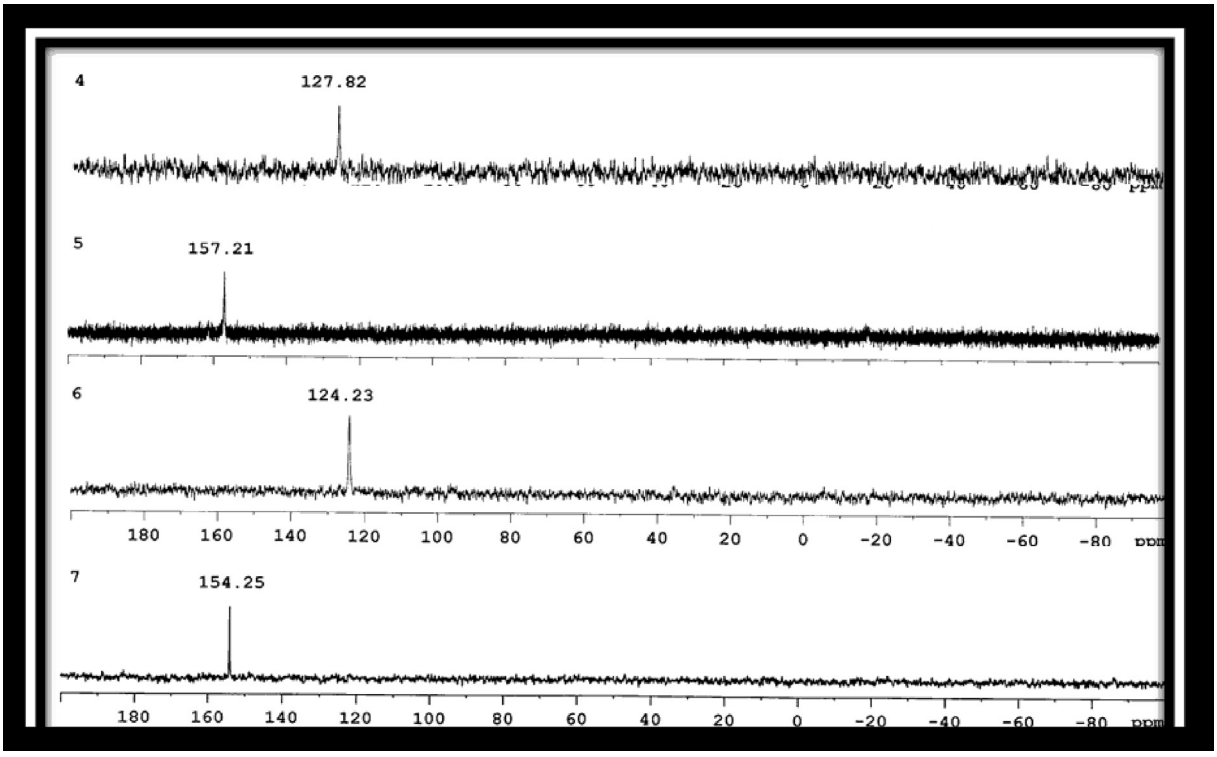


Fig. 4. The $^{31}P-\{^1H\}$ NMR spectra of the complexes [Ru((Ph$_2$PO)–C$_7$H$_{14}$N$_2$Cl)(η^6-benzene)Cl$_2$]Cl (**4**), [Ru((Cy$_2$PO)–C$_7$H$_{14}$N$_2$Cl)(η^6-benzene)Cl$_2$]Cl (**5**), [Ru((Ph$_2$PO)–C$_7$H$_{14}$N$_2$Cl)(η^6-*p*-cymene)Cl$_2$]Cl (**6**) and [Ru((Cy$_2$PO)–C$_7$H$_{14}$N$_2$Cl)(η^6-*p*-cymene)Cl$_2$]Cl (**7**) ($CDCl_3$).

the red compounds [Ru((Ph$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-*p*-cymene)Cl$_2$]Cl (**6**) and [Ru((Cy$_2$PO)–C$_7$H$_{14}$N$_2$Cl)(η^6-*p*-cymene)Cl$_2$]Cl (**7**), respectively, in high yields. The structures of the P-coordinated complexes **6** and **7** are supported by elemental analysis as well as spectroscopic data. The ^{1}H NMR spectral data of the complexes are consistent with the proposed structures and their ^{1}H NMR spectra are different from those of ligands **2** and **3**. Furthermore, the ^{1}H NMR spectra of the complexes display signals for the η^6-*p*-cymene group together with the resonances for the protons of the *P*-coordinated ligands. The arene signals are well resolved and show only H–H coupling, as found in previously reported mononuclear η^6-*p*-cymene compounds [57,58]. The ^{1}H and ^{13}C NMR spectra of the complexes display all the signals of the coordinated ligands. In the ^{1}H NMR spectra, aromatic CH protons of the *p*-cymene moiety generally give two signals. It is very well-known that the presence of one (broad) or two signals due to aromatic CH of *p*-cymene protons in the ^{1}H NMR spectra of **6** and **7** is consistent with a *Cs* symmetry of the complexes and free rotation of the arene (*p*-cymene) ligand [59,60]. Furthermore, The ^{1}H NMR spectra of **6** and **7** are characterized by isopropyl methyl doublets of the *p*-cymene groups, at δ 0.99 ppm (d, 6H, ^3J = 6.8 Hz) and δ 0.87 ppm (d, 6H, J = 6.5 Hz), respectively. In their $^{13}C-\{^1H\}$ NMR spectra, $J(^{31}P-^{13}C)$ coupling constants of the carbons of the phenyl rings are observed, which are consistent with the literature values [61,62]. As expected, the coupling between *i*-carbons and the phosphorus in **6** and **7** is relatively large, $^1J(^{31}P-^{13}C)$ 52.3 and 29.7 Hz, for *i*-P(C$_6$H$_5$)$_2$) and *C*H of P(C$_6$H$_{11}$)$_2$), respectively. The most relevant signals of the $^{13}C-\{^1H\}$ NMR spectra of the complexes are those of the arene ligands (*p*-cymene) (for details see Section 3). Although, single crystals of both complexes were obtained by slow diffusion of diethyl ether into a solution of the compound in dichloromethane over several days, unfortunately they lost their regular and transparent structures for X-ray diffraction analysis.

2.2. Thermal investigation (DTA)

The thermal behavior of the compounds [Ru((Ph$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-benzene)Cl$_2$]Cl (**4**), [Ru((Cy$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-benzene)Cl$_2$]Cl (**5**), [Ru((Ph$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-*p*-cymene)Cl$_2$]Cl (**6**) and [Ru((Cy$_2$PO)–C$_7$H$_{14}$N$_2$Cl)(η^6-*p*-cymene)Cl$_2$]Cl (**7**) was investigated in two steps under nitrogen and oxygen atmospheres with a heating rate of 20 °C min^{-1} over a temperature range 25–900 °C. The first step was applied with N_2 from 25 to 800 °C, and the second step proceeded under O_2 between 800 and 900 °C. The thermal stability of the compounds changes from one to another. It was seen that the compounds remained quite tough until 174, 164, 190 and 173 °C for **4**–**7**, respectively. The weight losses were calculated and evaluated with TA60 software in accordance with the peaks. Each of the computations with an exact percentage of the total was indicated on the thermograms, as depicted in the Supporting information (Figs. 5–8). The peaks pointing downwards on the graphic are endothermic and are due to the leaving substituted groups. The sudden increase of peaks after 800 °C is the result of burning organic fragments, such as imidazole, phenyl, cyclohexyl, *p*-cymene and benzene, which can be removed step by step.

2.3. Catalytic transfer hydrogenation of various ketones

The good catalytic performance and the higher structural permutability of phosphinite based transition metal complexes [63–65,38,66] prompted us to develop new Ru(II) complexes with well-shaped modified phosphinite ligands [67–70]. We paid particular attention to arene ligands [71], because (*i*) the spectator ligands automatically occupy three adjacent coordination sites of the ruthenium centre in an octahedral coordination environment, leaving three facial sites for other functions, (*ii*) arene ligands that are relatively weak electron donors may provide a unique reactivity on the metallic center, and (*iii*) the substitution pattern on the

ring is flexible. Complexes **4**–**7** were tested as catalysts in transfer hydrogenation of aromatic ketones in a 2-propanol solution.

First of all, complexes **4**–**7** were used as precatalysts, 2-propanol/KOH as the reducing system, and acetophenone as the model substrate. The results of the catalytic test reactions are listed in Table 3. At room temperature, no significant formation of 1-phenylethanol was observed (Table 3, Entries 2, 7, 12 and 17). Furthermore, as can be inferred from Table 3, the precatalysts as well as the presence of KOH are necessary to observe appreciable conversions. The base facilitates the formation of ruthenium alkoxide by abstracting a proton from the alcohol and subsequently the alkoxide undergoes β-elimination to give ruthenium hydride, which is an active species in this reaction [72–75]. As seen in Table 3, increasing the substrate-to-catalyst ratio does not cause a decrease in the conversion of the product in most cases. For instance, transfer hydrogenation of acetophenone could be achieved with 98% yield even when the substrate concentration was reduced from 0.1 to 0.05 or 0.01 M and the substrate-to-catalyst ratio reached 1000:1 at reflux temperature of the solvent, though with an increase in the reaction time (Table 3).When the reaction carried out with a substrate-to-catalyst ratio of 100:1 at reflux temperature, a smooth reduction of acetophenone into 1-phenylethanol occurred, with a conversion of up to 98% after 10 min for the reaction conducted with **5** and **7**, and 30 min for those with **4** and **6**. As seen in Table 3, a typical reduction reaction of acetophenone indicates that the reaction rate is independent of the type of arene moiety (benzene or *p*-cymene) bound to the metal center, despite its dependence on the alkyl substituents on the phosphorus atom. The results of the optimization studies demonstrate obviously that both complexes, [Ru($Cy_2POC_7H_{14}N_2Cl$)(η^6-benzene)Cl_2]Cl (**5**) and [Ru($Cy_2POC_7H_{14}N_2Cl$)(η^6-*p*-cymene)Cl_2]Cl (**7**), including a Cy moiety on the phosphorus atom, are active and efficient catalysts leading to nearly quantitative conversions. In addition, the catalytic efficiency was seen to be independent of the type of arene moiety.

Encouraged by the activities obtained in these preliminary studies, we next extended our investigations to include hydrogenation of substituted acetophenone derivatives. The results in Table 4 indicate that a range of acetophenone derivatives can be hydrogenated with good conversions. The catalytic reductions of the acetophenone derivatives were all carried out with the conditions optimized for acetophenone, and complexes **4**–**7** showed high activity for most of the ketones. The introduction of electron withdrawing substituents, attached to the aryl ring of the ketone, reduced the electron density of the C=O bond so that the activity was improved, giving rise to easier hydrogenation [76,77]. Comparing the catalytic performance to analogous complexes, the ionic liquid based Ru(II)–phosphinite complexes can possibly form a more stable catalytic transition state [78–81]. The catalytic activity of the complexes is higher than that recently reported for related half-sandwich complexes [82], and references therein].

Due to these efficient findings in the transfer hydrogenation of acetophenone derivatives, we next extended our investigations to include hydrogenation of various simple ketones. Examination of the catalytic activity of these complexes has shown that they are efficient catalysts, affording almost quantitative transformation of the ketones in short times (Table 5). For instance, hydrogenations of cyclohexanone and cyclopentanone could be achieved approximately in 20 min by [Ru($Cy_2POC_7H_{14}N_2Cl$)(η^6-benzene)Cl_2]Cl (**5**) and [Ru($Cy_2POC_7H_{14}N_2Cl$)(η^6-*p*-cymene)Cl_2]Cl (**7**). Conversion of methyl isobutyl ketone occurred in 1 h by **5** and **7**, while that of diethyl ketone occurred in 2 h by **5** and **7**. The catalytic activities of [Ru($Cy_2POC_7H_{14}N_2Cl$)(η^6-benzene)Cl_2]Cl (**5**) and [Ru($Cy_2POC_7H_{14}N_2Cl$)(η^6-*p*-cymene)Cl_2]Cl (**7**) were generally higher in the studied hydrogen transfer reactions.

We conducted further experiments to investigate the influence of the bulkiness of alkyl groups on the catalytic activity and the results are given in Table 6 (Entries 1–16). A variety of simple aryl alkyl ketones were transformed to the corresponding secondary alcohols, and it was found that the activity is highly dependent on the steric hindrance of the alkyl group. The reactivity gradually decreased by increasing the bulkiness of the alkyl groups [83–86].

Table 3
Transfer hydrogenation of acetophenone with 2-propanol catalyzed [Ru((Ph_2PO)-$C_7H_{14}N_2Cl$)(η^6-benzene)Cl_2]Cl, (**4**), [Ru((Cy_2PO)-$C_7H_{14}N_2Cl$)(η^6-benzene)Cl_2]Cl, (**5**), [Ru((Ph_2PO)-$C_7H_{14}N_2Cl$)(η^6-*p*-cymene)Cl_2]Cl, (**6**) and [Ru((Cy_2PO)-$C_7H_{14}N_2Cl$)(η^6-*p*-cymene)Cl_2]Cl, (**7**).

Entry	Catalyst	S/C/KOH	Time	Conversion (%)[f]	TOF (h^{-1})[g]
1	4[a]	100:1:5	30 min	97	194
2	4[b]	100:1:5	48 h	<5	–
3	4[c]	100:1	48 h	<5	–
4	4[d]	500:1:5	2 h	97	243
5	4[e]	1000:1:5	3 h	98	327
6	5[a]	100:1:5	10 min	98	588
7	5[b]	100:1:5	48 h	<5	–
8	5[c]	100:1	48 h	<5	–
9	5[d]	500:1:5	30 min	98	980
10	5[e]	1000:1:5	1 h	97	970
11	6[a]	100:1:5	30 min	95	190
12	6[b]	100:1:5	48 h	<5	–
13	6[c]	100:1	48 h	<5	–
14	6[d]	500:1:5	2 h	97	243
15	6[e]	1000:1:5	3 h	98	327
16	7[a]	100:1:5	10 min	97	582
17	7[b]	100:1:5	48 h	<5	–
18	7[c]	100:1	48 h	<5	–
19	7[d]	500:1:5	30 h	97	970
20	7[e]	1000:1:5	1 h	96	960

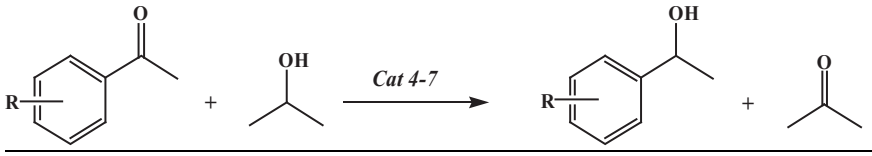
Reaction conditions:
[a] Refluxing in 2-propanol; acetophenone/Ru/KOH.
[b] At room temperature; acetophenone/Ru/KOH.
[c] Refluxing in 2-propanol; acetophenone/Ru, in the absence of base.
[d] Refluxing in 2-propanol; acetophenone/Ru/KOH.
[e] Refluxing in 2-propanol; acetophenone/Ru/KOH.
[f] Determined by GC (three independent catalytic experiments).
[g] Referred at the reaction time indicated in column; TOF= (mol product/mol Ru(II)Cat.) × h^{-1}.

3. Experimental

3.1. Materials and methods

Unless otherwise stated, all reactions were carried out under an atmosphere of argon using conventional Schlenk glass-ware, solvents were dried using established procedures and distilled under argon immediately prior to use. Analytical grade and deuterated solvents were purchased from Merck. PPh_2Cl, PCy_2Cl, epichlorohydrin and 1-methylimidazole were purchased from Fluka and used as received. The starting materials [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ [87,88] and [Ru(η^6-benzene)(μ-Cl)Cl]$_2$ [89] were prepared according to literature procedures. FTIR spectra were recorded on an ATR apparatus on a Perkin Elmer Spectrum 100 Fourier Transform spectrophotometer and thermogravimetric analysis of the catalysts was carried out on a Shimadzu DSC 60A thermal analyzer up to 800–900 °C at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere. ^1H (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{31}P–{^1H} NMR (162.0 MHz) spectra were recorded on a Bruker AV400 spectrometer, with δ referenced to external TMS and 85% H_3PO_4 respectively. Elemental analysis of carbon, hydrogen and nitrogen was carried out on a Costech Combustion System CHNS-O instrument. Melting points were recorded by a Gallenkamp Model apparatus with open capillaries.

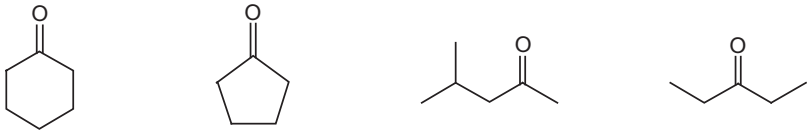
Table 4
Transfer hydrogenation results for substituted acetophenones with the catalyst systems, [Ru((Ph$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-benzene)Cl$_2$]Cl, (**4**), [Ru((Cy$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-benzene)Cl$_2$]Cl, (**5**), [Ru((Ph$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-*p*-cymene)Cl$_2$]Cl, (**6**) and [Ru((Cy$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-*p*-cymene)Cl$_2$]Cl, (**7**).[a]



Entry	R	Time	Conversion (%)[b]	TOF(h^{-1})[c]
Cat: Ru(II) complex, ***4***				
1	4-F	15 min	97	388
2	4-Cl	15 min	98	392
3	4-Br	30 min	95	190
4	2-MeO	1 h	97	97
5	4-MeO	45 min	96	128
Cat: Ru(II) complex, ***5***				
6	4-F	5 min	99	1188
7	4-Cl	5 min	97	1164
8	4-Br	10 min	98	588
9	2-MeO	20 min	95	285
10	4-MeO	15 min	96	384
Cat: Ru(II) complex, ***6***				
11	4-F	15 min	96	384
12	4-Cl	15 min	97	388
13	4-Br	30 min	97	194
14	2-MeO	1 h	98	98
15	4-MeO	45 min	96	128
Cat: Ru(II) complex, ***7***				
16	4-F	5 min	98	1176
17	4-Cl	5 min	97	1164
18	4-Br	10 min	97	582
19	2-MeO	20 min	96	288
20	4-MeO	15 min	96	384

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), 2-propanol (5 mL), KOH (0.025 mmol%), 82 °C, the concentration of acetophenone derivatives is 0.1 M.
[b] Purity of compounds is checked by ^{1}H NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone.
[c] TOF = (mol product/mol Cat.) × h^{-1}.

Table 5
Transfer hydrogenation of various simple ketones with 2-propanol catalyzed by [Ru((Ph$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-benzene)Cl$_2$]Cl, (**4**), [Ru((Cy$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-benzene)Cl$_2$]Cl, (**5**), [Ru((Ph$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-*p*-cymene)Cl$_2$]Cl (**6**) and [Ru((Cy$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-*p*-cymene)Cl$_2$]Cl, (**7**).[a]

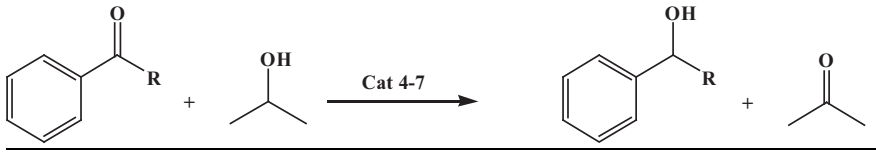


a **b** **c** **d**

Entry	Cat.	Substrate	Time	Conversion (%)[b]	TOF (h^{-1})[c]
1	4	a	60 min	96	96
2	4	b	60 min	97	97
3	4	c	3 h	98	33
4	4	d	6 h	98	16
5	5	a	20 min	97	291
6	5	b	20 min	99	297
7	5	c	1 h	98	98
8	5	d	2 h	96	48
9	6	a	60 min	99	99
10	6	b	60 min	98	98
11	6	c	3 h	96	32
12	6	d	6 h	97	16
13	7	a	20 min	96	288
14	7	b	20 min	98	297
15	7	c	1 h	96	96
16	7	d	2 h	99	50

[a] Refluxing in 2-propanol; ketone/Ru/KOH, 100:1:5.
[b] Determined by GC (three independent catalytic experiments).
[c] Purity of compounds is checked by ^{1}H NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone.

Table 6
Transfer hydrogenation results for substituted alkyl phenyl ketones with the catalyst systems [Ru((Ph$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-benzene)Cl$_2$]Cl, (**4**), [Ru((Cy$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-benzene)Cl$_2$]Cl, (**5**), [Ru((Ph$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-*p*-cymene)Cl$_2$]Cl, (**6**) and [Ru((Cy$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-*p*-cymene)Cl$_2$]Cl, (**7**).[a]



Entry	R	Time	Conversion (%)[b]	TOF(h^{-1})[c]
Cat: Ru(II) complex, ***4***				
1	ethyl	40 min	97	146
2	propyl	60 min	98	98
3	iso-propyl	2 h	95	48
4	ter-butyl	3 h	98	33
Cat: Ru(II) complex, ***5***				
5	ethyl	15 min	95	380
6	propyl	20 min	97	291
7	iso-propyl	40 min	98	147
8	ter-butyl	1 h	96	96
Cat: Ru(II) complex, ***6***				
9	ethyl	40 min	96	144
10	propyl	60 min	98	98
11	iso-propyl	2 h	98	49
12	ter-butyl	3 h	99	33
Cat: Ru(II) complex, ***7***				
13	ethyl	15 min	98	392
14	propyl	20 min	97	291
15	iso-propyl	40 min	96	144
16	ter-butyl	1 h	95	95

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), 2-propanol (5 mL), KOH (0.025 mmol%), 82 °C, respectively, the concentration of alkyl phenyl ketones is 0.1 M.
[b] Purity of compounds is checked by ^{1}H NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone.
[c] TOF = (mol product/mol Cat.) × h^{-1}.

3.2. Transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen transfer reaction: a solution of the complexes [Ru((Ph$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-*arene*)Cl$_2$]Cl and [Ru((Ph$_2$PO)-C$_7$H$_{14}$N$_2$Cl)(η^6-*arene*)Cl$_2$]Cl {*arene*: benzene **4**, **5**; *p*-cymene **6**, **7**} (0.005 mmol), KOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed 2-propanol (5 mL) was refluxed until the reactions were completed. Then, a sample of the reaction mixture was taken off, diluted with acetone and analyzed immediately by GC. The conversions are related to the residual unreacted ketone. GC analyses were performed a Shimadzu 2010 Plus Gas Chromatograph equipped with a capillary column (5% biphenyl, 95% dimethylsiloxane) (30 m × 0.32 mm × 0.25 μm). The GC parameters for transfer hydrogenation of the ketones were as follows: initial temperature, 50 °C; initial time, hold min 1 min; solvent delay, 4.48 min; temperature ramp 15 °C/min; final temperature, 270 °C, hold min 5 min; final time, 20.67 min; injector port temperature, 200 °C; detector temperature, 200 °C, injection volume, 2.0 μL.

3.3. Synthesis of the new compounds

3.3.1. Synthesis of 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride [C$_7$H$_{15}$N$_2$OCl]Cl (*1*)

To a stirred solution of 1-methylimidazole (20.733 g, 250 mmol) in ethanol (40 mL) at room temperature was carefully added concentrated hydrochloric acid (20.95 mL, 255 mmol). *Caution: neutralization of a base with a strong acid is highly exothermic.* After addition of acid, the reaction mixture was cooled to room temperature and epichlorohydrin (24.057 g, 260 mmol) was added dropwise with stirring, while maintaining the temperature at 25 °C. The reaction vessel was then sealed and stirred at room temperature for approximately 30 h. The solvent was removed under reduced pressure on heating at 70 °C, followed by heating under high vacuum, to yield a liquid that became more viscous upon extensive drying, and this was was recrystallized from ethylacetate at 0 °C. The precipitated product was filtered and dried in vacuo yielding **1** as an off-white solid. Yield: 52.52 g, 98.1%; M.p.: 94–95 °C; ^{1}H NMR (400.1 MHz, DMSO-d_6, ppm) δ: 9.26 (s, 1H, (CH$_3$)NC*H*N–), 7.78 and 7.76 (2xs, 2H, –NC*HCH*N–), 6.19 (d, 1H, ^3J = 5.0 Hz, –CHO*H*), 4.42 (m, 1H, NCH_2, (a)), 4.19 (m, 1H, NCH_2, (b)), 4.05 (br, 1H, –C*H*OH), 3.88 (s, 3H, CH_3N), 3.65 (d, 2H, ^3J = 3.6 Hz, –CH_2Cl); ^{13}C NMR (100.6 MHz, DMSO-d_6, ppm) δ: 36.20 (N*C*H$_3$), 46.94 (–*C*H$_2$Cl), 52.45 (N*C*H$_2$), 69.07 (–*C*HOH), 123.47, 123.70 (–NCHCHN–), 137.62 ((CH$_3$)NCHN–); assignment was based on the ^{1}H–^{13}C HETCOR, DEPT and ^{1}H–^{1}H COSY spectra; IR, (KBr, cm^{-1}) *v*: 3357 (O-H), 3170, 3089 (aromatic C–H), 2985, 2856 (aliphatic C–H), 1575 (C=N), 1176 (C–N); *Anal.* for C$_7$H$_{15}$N$_2$OCl$_2$ (214.11 g/mol): Calc. C, 39.27; H, 7.06; N, 13.08. Found: C, 39.18; H, 6.99; N, 13.00%.

3.3.2. Synthesis of [(Ph$_2$PO)–C$_7$H$_{14}$N$_2$Cl]Cl (*2*)

A dry and degassed CH_2Cl_2 (20 ml) solution of 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride (**1**) (0.100 g, 0.47 mmol) under an argon atmosphere was cooled to −78 °C in an acetone and dry ice bath. To the cooled solution was added dropwise a hexane solution of *n*-BuLi (0.293 ml, 0.47 mmol). After the addition, the mixture was stirred at −78 °C for 1 h and then for another 30 min at room temperature. The reaction solution was cooled to −78 °C again and a solution of diphenylchlorophosphine (0.105 g, 0.47 mmol) in CH_2Cl_2 (10 ml) was added dropwise to the reaction medium. Stirring was continued for a further 1 h at −78 °C, then the cooling bath was removed and the mixture was stirred for another 1 h at room temperature. Precipitated lithium chloride was removed by filtration under argon and then the volatiles were evaporated *in vacuo* to leave a viscous oil of the phosphinite ligand **2**. Yield 0.180 g, 96.8%; ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 10.14 (s, 1H, –(CH$_3$)NC*H*N–), 7.13–7.78 (m, 12H,

$P(C_6H_5)_2$ + –NC*H*C*H*N–), 4.94 (m, 1H, NCH_2, (a)), 4.71 (br, 1H, –C*H*OP), 4.57 (m, 1H, NCH_2, (b)), 3.91 (m, 1H, –CH_2Cl, (a)), 3.85 (m, 1H, –CH_2Cl, (b)), 3.80 (s, 3H, NCH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 36.55 (NCH_3), 45.14 (–CH_2Cl), 52.52 (NCH_2), 78.45 (d, ^2J = 23.1 Hz, (–C*H*OP), 122.59, 122.90 (–NC*H*C*H*N–), 129.53 (d, $^3J_{31P-13C}$ = 10.1 Hz, *m*-P(C_6H_5)$_2$), 131.41 (*p*-P(C_6H_5)$_2$), 135.26 (d, $^2J_{31P-13C}$ = 19.6 Hz, *o*-P(C_6H_5)$_2$)), 138.17 ((CH$_3$)NC*H*N–), 140.65 (d, $^1J_{31P-13C}$ = 47.8 Hz, *i*-P(C_6H_5)$_2$); assignment was based on the ^{1}H–^{13}C HETCOR, DEPT and ^{1}H–^{1}H COSY spectra; ^{31}P–{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm) δ: 118.46 (s, OP*P*h$_2$); IR, (KBr, cm^{-1}) *v*: 3053 (aromatic C–H), 1434 (P–Ph), 1060 (O–P); *Anal.* Calc. for $C_{19}H_{24}N_2OCl_2P$ (398.29 g/mol): C, 57.30; H, 6.07; N, 7.03. Found: C, 57.18; H, 6.00; N, 6.96%.

3.3.3. Synthesis of [(Cy$_2$PO)–C$_7$H$_{14}$N$_2$Cl]Cl (**3**)

A dry and degassed CH_2Cl_2 (20 ml) solution of 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride (**1**) (0.100 g, 0.47 mmol) under an argon atmosphere was cooled to −78 °C in an acetone and dry ice bath. To the cooled solution was added dropwise a hexane solution of *n*-BuLi (0.293 ml, 0.47 mmol). After the addition, the mixture was stirred at −78 °C for 1 h and then for an additional 30 min at room temperature. The reaction solution was cooled to −78 °C again and a solution of dicyclohexylchlorophosphine (0.112 g, 0.47 mmol) in CH_2Cl_2 (10 ml) was added dropwise to the reaction medium. Stirring was continued for a further 1 h at −78 °C, then the cooling bath was removed and the mixture was stirred for 3 h at room temperature. Precipitated lithium chloride was removed by filtration under argon and then the volatiles were evaporated *in vacuo* to leave a viscous oil of the phosphinite ligand, **3**. Yield 0.183 g, 95.5%; ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 10.48 (s, 1H, –(CH$_3$)NC*H*N–), 7.64, 7.45 (2xs, 2H, –NC*H*C*H*N–), 4.84 (m, 1H, NCH_2, (a)), 4.53 (m, 1H, NCH_2, (b)), 4.16 (br, 1H, –C*H*OP), 4.10 (s, 3H, NCH_3), 3.83 (m, 1H, –CH_2Cl, (a)), 3.68 (m, 1H, –CH_2Cl, (b)), 1.00–1.95 (m, 22H, protons of P(C_6H_{11})$_2$; ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 26.20, 26.27, 26.64, 26.85, 26.98, 27.21 (*C*H$_2$ of P(C_6H_{11})$_2$), 36.77 (NCH$_3$), 37.20 (d, ^1J = 15.1 Hz, *C*H of P(C_6H_{11})$_2$), 44.05 (–*C*H$_2$Cl), 52.34 (NCH$_2$), 77.32 (d, ^2J = 22.7 Hz, –CHOP), 123.05, 123.43 (–NCHCHN–), 138.67 (–(CH$_3$)NCHN–); assignment was based on the ^{1}H–^{13}C HETCOR, DEPT and ^{1}H–^{1}H COSY spectra; ^{31}P–{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm) δ: 148.76 (s, O*P*Cy$_2$); IR, (KBr, cm^{-1}) *v*: 2923, 2850 (aliphatic C–H), 1446 (P–Cy), 1059 (O–P); *Anal.* Calc. for $C_{19}H_{36}N_2OCl_2P$ (410.39 g/mol): C, 55.61; H, 8.84; N, 6.83. Found: C, 55.56; H, 8.71; N, 6.70%.

3.3.4. Synthesis of [Ru((Ph$_2$PO)–C$_7$H$_{14}$N$_2$Cl)(η^6-benzene)Cl$_2$]Cl (**4**)

[Ru(η^6-benzene)(μ-Cl)Cl]$_2$ (0.063 g, 0.13 mmol) and [(Ph$_2$PO)–C$_7$H$_{14}$N$_2$Cl]Cl (**2**) (0.100 g, 0.25 mmol) were dissolved in 25 mL of dry CH_2Cl_2 under an argon atmosphere and stirred for 30 min at room temperature. The volume of the solvent was then reduced to 0.5 mL before addition of petroleum ether (10 mL). The precipitated product was filtered and dried in vacuo yielding **4** as a dark red solid. Yield 0.150 g, 92.1%; M.p.: 159–161 °C; ^{1}H NMR (400.1 MHz, DMSO-d_6, ppm) δ: 8.95 (s, 1H, –(CH$_3$)NC*H*N–), 7.44–7.88 (m, 12H, P(C_6H_5)$_2$ + –NC*H*C*H*N–), 5.55 (s, 6H, aromatic protons of benzene), 5.11 (br, 1H, –C*H*OP), 4.37 (m, 2H, NCH_2), 3.82 (s, 3H, NCH_3), 3.50 (br, 2H, –CH_2Cl); ^{13}C NMR (100.6 MHz, DMSO-d_6, ppm) δ: 36.29 (NCH$_3$), 44.84 (–CH$_2$Cl), 52.56 (NCH$_2$), 74.96 (d, ^2J = 23.2 Hz, –CHOP), 88.10 (aromatic carbons of benzene), 123.54, 123.82 (–NCHCHN–), 128.76 (d, $^3J_{31P-13C}$ = 9.4 Hz, *m*-P(C_6H_5)$_2$), 132.98 (d, $^4J_{31P-13C}$ = 3.0 Hz, *p*-P(C_6H_5)$_2$), 133.52 (d, $^2J_{31P-13C}$ = 20.1, *o*-P(C_6H_5)$_2$)), 137.10 (–(CH$_3$)NCHN–), 139.49 (d, $^1J_{31P-13C}$ = 52.3 Hz, *i*-P(C_6H_5)$_2$); assignment was based on the ^{1}H–^{13}C HETCOR, DEPT and ^{1}H–^{1}H COSY spectra; ^{31}P–{^{1}H} NMR (162.0 MHz, DMSO-d_6, ppm) δ: 97.68; ($CDCl_3$, ppm) δ: 127.82 (s, Ru–OP*P*h$_2$); IR, (KBr, cm^{-1}) *v*: 3064 (aromatic C–H), 1435 (P–Ph), 1047 (O–P), 532 (Ru–P); *Anal.* Calc. for $C_{25}H_{30}N_2OCl_4PRu$ (648.38 g/mol): C, 46.31; H, 4.66; N, 4.32. Found: C, 46.22; H, 4.57; N, 4.27%.

3.3.5. Synthesis of [Ru((Cy$_2$PO)–C$_7$H$_{14}$N$_2$Cl)(η^6-benzene)Cl$_2$]Cl, (**5**)

[Ru(η^6-*p*-benzene)(μ-Cl)Cl]$_2$ (0.061 g, 0.12 mmol) and [(Cy$_2$PO)–C$_7$H$_{14}$N$_2$Cl]Cl (**3**) (0.100 g, 0.24 mmol) were dissolved in 25 mL of dry CH_2Cl_2 under an argon atmosphere and stirred for 30 min at room temperature. The volume of the solvent was then reduced to 0.5 mL before addition of petroleum ether (10 mL). The precipitated product was filtered and dried in vacuo yielding **5** as a dark red solid. Yield 0.141 g, 87.6%; M.p.: 142–144 °C. ^{1}H NMR (400.1 MHz, DMSO-d_6, ppm) δ: 9.02 (s, 1H, –(CH$_3$)NC*H*N–), 7.71, 7.54 (2xs, 2H, –NC*H*C*H*N–), 5.96 (s, 6H, aromatic protons of benzene), 5.20 (br, 1H, –C*H*OP), 4.32 (br, 2H, NCH_2), 3.82 (s, 3H, NCH_3), 3.54 (br, 2H, –CH_2Cl), 2.42 (m, 2H, C*H* of P(C_6H_{11})$_2$), 1.29–1.78 (m, 20H, CH_2 of P(C_6H_{11})$_2$); ^{13}C NMR (100.6 MHz, DMSO-d_6, ppm) δ: 26.85, 26.94, 27.05, 28.08, 28.28, 28.56 (*C*H$_2$ of P(C_6H_{11})$_2$), 36.39 (NCH$_3$), 45.75 (–CH$_2$Cl), 46.93 (d, ^1J = 28.5 Hz, *C*H of P(C_6H_{11})$_2$), 49.98 (NCH$_2$), 73.60 (d, ^2J = 22.9 Hz, –CHOP), 88.11 (aromatic carbons of benzene), 123.06, 124.14 (–NCHCHN–), 137.59 (–(CH$_3$)NCHN–); assignment was based on the ^{1}H–^{13}C HETCOR, DEPT and ^{1}H–^{1}H COSY spectra; ^{31}P–{^{1}H} NMR (162.0 MHz, DMSO-d_6,ppm) δ: 159.24; ($CDCl_3$-d_1, ppm) δ: 157.21 (s, Ru–OP*C*y$_2$); IR, (KBr, cm^{-1}) *v*: 2927, 2851 (aliphatic C–H), 1435 (P–Cy), 1059 (O–P), 520 (Ru–P); *Anal.* Calc. for $C_{25}H_{42}N_2OCl_4PRu$ (660.48 g/mol): C, 45.46; H, 6.41; N, 4.24. Found: C, 45.38; H, 6.30; N, 4.16%.

3.3.6. Synthesis of [Ru((Ph$_2$PO)–C$_7$H$_{14}$N$_2$Cl)(η^6-*p*-cymene)Cl$_2$]Cl (**6**)

[Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.077 g, 0.13 mmol) and [(Ph$_2$PO)–C$_7$H$_{14}$N$_2$Cl]Cl (**2**) (0.100 g, 0.25 mmol) were dissolved in 25 mL of dry CH_2Cl_2 under an argon atmosphere and stirred for 30 min at room temperature. The volume of the solvent was then reduced to 0.5 mL before addition of petroleum ether (10 mL). The precipitated product was filtered and dried in vacuo yielding **6** as a clear red solid. Yield 0.162 g, 91.6%; M.p.: 110–112 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 9.53 (s, 1H, –(CH$_3$)NC*H*N–), 7.14–7.93 (m, 12H, P(C_6H_5)$_2$ + –NC*H*C*H*N–), 5.43 (br, 2H, aromatic protons of *p*-cymene), 5.23 (br, 2H, aromatic protons of *p*-cymene), 4.81 (br, 1H, –C*H*OP), 4.61 (br, 1H, NCH_2, (a)), 4.48 (br, 1H, NCH_2, (b)), 3.94 (s, 3H, NCH_3), 3.42 (br, 2H, –CH_2Cl), 2.46 (m, 1H, C*H* of *p*-cymene), 1.83 (s, 3H, CH_3Ph of *p*-cymene), 0.99 (d, 6H, ^3J = 6.8 Hz, (CH_3)$_2$CHPh of *p*-cymene); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 17.22 (*C*H$_3$Ph of *p*-cymene), 22.16, 22.23 ((CH$_3$)$_2$CHPh of *p*-cymene), 30.01 (*C*H of *p*-cymene), 37.36 (NCH$_3$), 44.57 (CH$_2$Cl), 50.92 (NCH$_2$), 75.11 (d, ^2J = 22.9 Hz, –CHOP), 86.77 (d, $^2J_{31P-13C}$ = 5.0 Hz, aromatic carbons of *p*-cymene), 88.89 (d, $^2J_{31P-13C}$ = 7.0 Hz, aromatic carbons of *p*-cymene), 89.35 (d, $^2J_{31P-13C}$ = 4.0 Hz, aromatic carbons of *p*-cymene), 92.56 (d, $^2J_{31P-13C}$ = 6.0 Hz, aromatic carbons of *p*-cymene), 96.31, 111.15 (quaternary carbons of *p*-cymene), 122.60, 123.17 (–NCHCHN–), 128.34 (d, $^3J_{31P-13C}$ = 10.1 Hz, *m*-P(C_6H_5)$_2$)), 131.91 (d, $^4J_{31P-13C}$ = 6.1 Hz, *p*-P(C_6H_5)$_2$), 133.84 (d, $^2J_{31P-13C}$ = 12.6 Hz, *o*-P(C_6H_5)$_2$), 137.87 (d, $^1J_{31P-13C}$ = 52.3 Hz, *i*-P(C_6H_5)$_2$), 139.70 (–(CH$_3$)NCHN–); assignment was based on the ^{1}H–^{13}C HETCOR, DEPT and ^{1}H–^{1}H COSY spectra; ^{31}P–{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm) δ: 124.23 (s, Ru–OP*P*h$_2$); IR, (KBr, cm^{-1}) *v*: 3053 (aromatic C–H), 1435 (P–Ph), 1047 (O–P), 532 (Ru–P); *Anal.* Calc. for $C_{29}H_{38}N_2OCl_4PRu$ (704.49 g/mol): C, 49.44; H, 5.44; N, 3.98. Found: C, 49.34; H, 5.32; N, 3.89%.

3.3.7. Synthesis of [Ru((Cy$_2$PO)–C$_7$H$_{14}$N$_2$Cl)(η^6-*p*-cymene)Cl$_2$]Cl (**7**)

[Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.075 g, 0.12 mmol) and [(Cy$_2$PO)–C$_7$H$_{14}$N$_2$Cl]Cl (**3**) (0.100 g, 0.24 mmol) were dissolved in 25 mL of dry CH_2Cl_2 under an argon atmosphere and stirred for 30 min at room temperature. The volume of the solvent was then reduced to 0.5 mL before addition of petroleum ether (10 mL). The precipitated product was filtered and dried in vacuo yielding

7 as a clear red solid. Yield 0.163 g, 93.3%; M.p.: 106–108 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 9.81 (s, 1H, –(CH_3)NC*H*N–), 7.66, 7.08 (2xs, 2H, –NC*H*C*H*N–), 5.64 (d, 2H, ^3J = 3.8 Hz, aromatic protons of *p*-cymene), 5.61 (d, 2H, ^3J = 3.8 Hz, aromatic protons of *p*-cymene), 5.35 (m, 1H, –C*H*OP), 4.72 (m, 1H, NCH_2, (a)), 4.43 (m, 1H, NCH_2, (b)), 4.02 (s, 3H, NCH_3), 3.83 (m, 1H, –CH_2Cl, (a)), 3.26 (m, 1H, –CH_2Cl, (b)), 2.81 (m, 1H, –C*H* of *p*-cymene), 2.12 (s, 3H, CH_3Ph of *p*-cymene), 1.28–1.36 (m, 22H, P$(C_6H_{11})_2$), 0.87 (d, 6H, ^3J = 6.5 Hz, $(CH_3)_2$CHPh of *p*-cymene); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 18.77 (CH_3Ph of *p*-cymene), 22.33, 22.48 (($CH_3)_2$ CHPh of *p*-cymene), 26.25, 26.94, 27.21, 27.85, 28.48, 29.06 (CH_2 of P$(C_6H_{11})_2$), 30.83 (*C*H of *p*-cymene), 37.38 (NCH_3), 46.06 (–CH_2Cl), 46.35 (d, ^1J = 29.7 Hz, *C*H of P$(C_6H_{11})_2$), 49.79 (NCH_2), 74.50 (d, ^2J = 24.2 Hz, –*C*HOP), 84.86, 90.33 (aromatic carbons of *p*-cymene), 96.28, 110.99 (quaternary carbons of *p*-cymene), 122.40, 122.42 (–NC*H*C*H*N–), 139.09 (–(CH_3)NC*H*N–); assignment was based on the ^{1}H–^{13}C HETCOR, DEPT and ^{1}H–^{1}H COSY spectra; ^{31}P–{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm) δ: 154.25 (s, Ru–O*P*Cy_2); IR, (KBr, cm^{-1}) ν: 2926, 2852 (aliphatic C–H), 1446 (P–Cy), 1057 (O–P), 528 (Ru–P); *Anal.* Calc. for $C_{29}H_{50}N_2OCl_4PRu$ (716.58 g/mol): C, 48.61; H, 7.03; N, 3.91. Found: C, 48.53; H, 6.92; N, 3.83%.

3.4. X-ray diffraction structure analysis

The single crystal data of 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride (**1**) were collected using a BRUKER APEX II CCD detector with graphite crystal monochromated Mo Kα radiation from a K780 X-ray generator applying 50 kV and 40 mA. The structure was solved by direct methods using SHELXS-97 and refined against F^2 by full matrix least-squares using SHELXL-97 [90]. The X-ray diffraction study of the crystal reveals that it belongs to monoclinic system with space group *P*2(1). The dimensions of the unit cell can be denoted as 4.90220 Å for (*a*), 14.1086 Å for (*b*), 7.29760 Å for (*c*). Hydrogen atoms attached to carbon were placed in calculated positions. Anisotropic displacement parameters, which were applied to all non-hydrogen atoms, were refined. The crystal data of the structure are given in Table 1. The molecular drawings of **1** were obtained with Mercury 3.0. The acquired results of the X-ray structure determination are presented in Tables 1 and 2 and Figs. 1 and 2.

4. Conclusion and perspectives

In this work, the preparation of four new Ru(II)–*arene* complexes based on ionic liquid phosphinite ligands is reported for the first time. These complexes have also exhibited promising catalytic activity in the transfer hydrogenation reaction of ketones in 2-propanol. Furthermore, the influences of arene rings and alkyl groups on the phosphorus atom in the catalytic transfer hydrogenation of aromatic ketones were also examined, and it was seen that the catalytic activities depend on the groups (phenyl and cyclohexyl) on the phosphorus atom, while they are independent on the arene moieties bound to metal center. Further studies of other transition metal complexes of this ligand are in progress and will be reported in due course.

Acknowledgements

Partial support of this work by The Scientific and Technological Research Council of Turkey and Dicle University Research Fund (Project number: DÜAPK 05-FF-27), and the analysis conducted by Dicle University Science Faculty and Technology Research Center (DUBTAM) are gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.05.079.

References

[1] T. Welton, Chem. Rev. 99 (1999) 2071.
[2] K.R. Seddon, J. Chem. Technol. Biotechnol. 68 (1997) 351.
[3] Y. Chauvin, H. Olivier-Bourbigou, ChemTech 25 (1995) 26.
[4] R.T. Carlin, J.S. Wilkes, in: G. Mamantov, A. Popov (Eds.), Advances in Non-aqueous Chemistry, VCH, New York, 1994.
[5] M. Freemantle, Chem. Eng. News 15 (2000) 37. and 4 (1999) 23.
[6] H. Carmichael, Chem. Br. 1 (2000) 36.
[7] S.V. Malhotra, H. Zhao, Phys. Chem. Liq. 42 (2004) 215.
[8] Y. Xiao, S.V. Malhotra, J. Organomet. Chem. 690 (2005) 3609.
[9] P. Nockemann, M. Pellens, K. Van Hecke, L. Van Meervelt, J. Wouters, B. Thijs, E. Vanecht, T.N. Parac-Vogt, H. Mehdi, S. Schaltin, J. Fransaer, S. Zahn, B. Kirchner, K. Binnemans, Chem. Eur. J. 16 (2010) 1849.
[10] C. Chiappe, C.S. Pomelli, U. Bardi, S. Caporali, Phys. Chem. Chem. Phys. 14 (2012) 5045.
[11] (a) T. Welton, Coord. Chem. Rev. 248 (2004) 2459;
(b) J.P. Hallett, T. Welton, Chem. Rev. 111 (2011) 3508.
[12] J.P. Hallett, T. Welton, Chem. Rev. 111 (2011) 3508.
[13] A. Corma, H. Garcia, A. Leyva, Tetrahedron 60 (2004) 8553.
[14] S. Lee, Y.J. Zhang, J.Y. Piao, H. Yoon, C.E. Song, J.H. Choi, J. Hong, Chem. Commun. (2003) 2624.
[15] T.J. Geldbach, P.J. Dyson, J. Am. Chem. Commun. 126 (2004) 8114.
[16] C. Baleizao, B. Gigante, H. Garcia, A. Corma, Tetrahedron Lett. 44 (2003) 6813.
[17] M.D. Rudd, M.A. Creighton, J.A. Kautz, Polyhedron 23 (2004) 1923.
[18] K.G. Gaw, M.B. Smith, J.W. Steed, J. Organomet. Chem. 664 (2002) 294.
[19] F. Agbossou, J.-F. Carpentier, F. Hopiot, I. Suisse, A. Mortreux, Coord. Chem. Rev. 178–180 (1998) 1615.
[20] H.J. Kreuzfelt, C. Döbler, J. Mol. Catal. A 136 (1998) 105.
[21] F. Agbossou-Niedercorn, I. Suisse, Coord. Chem. Rev. 242 (2003) 145.
[22] P. Bergamini, V. Bertolasi, F. Milani, Eur. J. Inorg. Chem. (2004) 1277.
[23] G.D. Cuny, S.L. Buchwald, J. Am. Chem. Soc. 115 (1993) 2066.
[24] Z. Csok, G. Szalontai, G. Czira, L. Kollar, J. Organomet. Chem. 570 (1998) 23.
[25] R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, Wiley-Interscience, New York, 2001.
[26] H.B. Kagan, M. Sasaki, Transition Metals for Organic Synthesis, Wiley-VCH, Weinheim, 1998.
[27] P.W. Galka, H –B. Kraatz, J. Organomet. Chem. 674 (2003) 24.
[28] R.A.W. Johnstone, A.H. Wilby, I.D. Entwistle, Chem. Rev. 85 (1985) 129.
[29] M. Yiğit, B. Yiğit, I. Özdemir, E. Çetinkaya, B. Çetinkaya, Appl. Organometal. Chem. 20 (2006) 322.
[30] R. Noyori, H. Takaya, Acc. Chem. Res. 23 (1990) 345.
[31] S. Ram, R.E. Ehrenkaufer, Synthesis (1988) 91.
[32] O. Pamies, J.-E. Backvall, Chem. Eur. J. 23 (7) (2001) 5052.
[33] R. Noyori, T. Ohkuma, M. Kitamura, H. Takaya, N. Sayo, H. Kumobayashi, S. Akutagawa, J. Am. Chem. Soc. 109 (1987) 5856.
[34] T. Ohkuma, H. Ooka, S. Hashiguchi, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 117 (1995) 2675.
[35] A. Kilic, F. Durap, M. Aydemir, A. Baysal, E. Taş, J. Organomet. Chem. 693 (2008) 2835.
[36] H. Shimizu, I. Nagasaki, T. Satio, Tetrahedron 61 (2005) 5405.
[37] M. Aydemir, F. Durap, A. Baysal, N. Meric, A. Buldağ, B. Gümgüm, S. Özkar, L.T. Yıldırım, J. Mol. Catal. A 326 (2010) 75.
[38] M. Aydemir, A. Baysal, N. Meric, B. Gümgüm, J. Organomet. Chem. 694 (2009) 2488.
[39] M. Aydemir, N. Meric, A. Baysal, Y. Turgut, C. Kayan, S. Seker, M. Toğrul, B. Gümgüm, J. Organomet. Chem. 696 (2011) 1541.
[40] A. Baysal, M. Aydemir, F. Durap, B. Gümgüm, S. Özkar, L.T. Yıldırım, Polyhedron 26 (2007) 3373.
[41] M. Aydemir, A. Baysal, F. Durap, B. Gümgüm, S. Özkar, L.T. Yıldırım, Appl. Organomet. Chem. 23 (11) (2009) 467.
[42] M.S. Balakrishna, R. McDonald, Inorg. Chem. Commun. 5 (2002) 782.
[43] P. Bergamini, V. Bertolasi, M. Cattabriga, V. Ferretti, U. Loprieno, N. Mantovani, L. Marvelli, Eur. J. Inorg. Chem. (2003) 918.
[44] R. Ceron-Camacho, V. Gomez-Benitez, R. Le Lagadec, D. Morales-Morales, R.A. Toscano, J. Mol. Catal. A 247 (2006) 124.
[45] I.D. Kostas, Inorg. Chim. Acta 355 (2003) 424.
[46] E.A. Broger, W. Burkart, M. Hennig, M. Scalone, R. Schmid, Tetrahedron Asymmetry 9 (1998) 4043.
[47] E. Hauptman, R. Shapiro, W. Marshall, Organometallics 17 (1998) 4976.
[48] K. Ruhlan, P. Gigler, E. Herdweck, J. Organomet. Chem. 693 (2008) 874.
[49] M. Hariharasarma, C.H. Lake, C.L. Watkins, M.G. Gray, J. Organomet. Chem. 580 (1999) 328.
[50] G. Esquius, J. Pons, R. Yanez, J. Ros, R. Mathieu, N. Lugan, B. Donnadieu, J. Organomet. Chem. 667 (2003) 126.
[51] Z. Fei, R. Scopelliti, P.J. Dyson, Inorg. Chem. 42 (2003) 2125.
[52] Z. Fei, R. Scopelliti, P.J. Dyson, Eur. J. Inorg. Chem. (2004) 530.
[53] H. Le Bozec, D. Touchard, P.H. Dixneuf, Adv. Organomet. Chem. 29 (1989) 163.

[54] A.M. Maj, K.M. Pietrusiewicz, I. Suisse, F. Agbossou, A. Mortreux, Tetrahedron Asymmetry 10 (1999) 831.
[55] F. Majoumo, P. Lönnecke, O. Kühl, E. Hey-Hawkins, Z. Anorg. Allg. Chem. 630 (2004) 305.
[56] M.A. Bennet, G.B. Robertson, A.K. Smith, J. Organomet. Chem. 43 (1972) C41.
[57] H. Yang, N. Lugan, R. Mathieu, Ann. Quim. Int. Ed. 93 (1997) 28.
[58] R. Tribo, S. Munoz, J. Pons, R. Yanez, A. Alvarez-Larena, J.F. Piniella, J. Ros, J. Organomet. Chem. 690 (2005) 4072.
[59] E. de la Encarnacion, J. Pons, R. Yanez, J. Ros, Inorg. Chim. Acta 358 (2005) 3272.
[60] I. Moldes, E. de la Encarnacion, J. Ros, A. Alvarez-Larena, J.F. Piniella, J. Organomet. Chem. 566 (1998) 165.
[61] P.Le Gendre, M. Offenbecher, C. Bruneau, P.H. Dixneuf, Tetrahedron Asymmetry 9 (1998) 2279.
[62] Q. Zhang, G. Hua, P. Bhattacharrya, A.M.Z. Slawin, J.D. Woollins, J. Chem. Soc., Dalton Trans. (2003) 3250.
[63] M. Alvarez, N. Lugan, R. Mathieu, J. Chem. Soc., Dalton Trans. (1994) 2755.
[64] H. Yang, M. Alvarez, N. Lugan, R. Mathieu, J. Chem. Soc., Chem. Commun. (1995) 1721.
[65] G. Venkatachalam, R. Ramesh, Inorg. Chem. Commun. 8 (2005) 1009.
[66] M. Aydemir, A. Baysal, N. Meric, C. Kayan, M. Toğrul, B, Gümgüm, Appl. Organomet. Chem. 24 (2010) 215.
[67] F. Durap, M. Aydemir, D. Elma, A. Baysal, Y. Turgut, C. R. Chimie 16 (2013) 363.
[68] M. Aydemir, F. Durap, C. Kayan, A. Baysal, Y. Turgut, Synlett 23 (2012) 2777.
[69] M. Aydemir, N. Meric, F. Durap, A. Baysal, M. Toğrul, J. Organomet. Chem. 695 (2010) 1392.
[70] M. Aydemir, N. Meric, A. Baysal, B. Gümgüm, M. Toğrul, Y. Turgut, Tetrahedron Asymmetry 21 (2010) 703.
[71] E.L. Muetterties, J.R. Bleeke, E.J. Wucherer, T.A. Albright, Chem. Rev. 82 (1982) 499.
[72] M.J. Palmer, M. Will, Tetrahedron Asymmetry 10 (1999) 2045.
[73] E.P. Kelson, P.P. Phengsy, J. Chem. Soc., Dalton Trans. (2000) 4023.
[74] H. Zhang, B.C. Yang, Y.Y. Li, Z.R. Donga, J.X. Gao, H. Nakamura, K. Murata, T. Ikariya, Chem. Commun. (2003) 142.
[75] J. Hannedouche, G.J. Clarkson, M. Wills, J. Am. Chem. Soc. 126 (2004) 986.
[76] J.W. Faller, A.R. Lavoie, Organometallics 20 (2001) 5245.
[77] P. Pelagatti, M. Carcelli, F. Calbiani, C. Cassi, L. Elviri, C. Pelizzi, U. Rizzotti, D. Rogolino, Organometallics 24 (2005) 5836.
[78] C. Standfest-Hauser, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, L. Xiao, W. Weissensteiner, J. Chem. Soc., Dalton Trans. (2001) 2989.
[79] A.M. Maj, K.M. Pietrusiewicz, I. Suisse, F. Agbossou, A. Mortreux, J. Organomet. Chem. 626 (2001) 157.
[80] K.-J. Haack, S. Hashiguchi, A. Fuji, T. Ikariya, R. Noyori, Angew. Chem. Int. Ed. Engl. 36 (1997) 285.
[81] A. Caballero, F.A. Jalon, B.R. Manzano, G. Espino, M. Perez-Manrique, A. Mucientes, F.J. Poblete, M. Maestro, Organometallics 23 (2004) 5694.
[82] P. Dani, T. Karlen, R.A. Gossage, S. Gladialli, G. van Koten, Angew. Chem. Int. Ed. Engl. 39 (2000) 743.
[83] J.-X. Gao, X.-D. Yi, P.-P. Xu, C.-L. Tang, H.-L. Wan, T. Ikariya, J. Organomet. Chem. 592 (1999) 290.
[84] J.-X. Gao, H. Zhang, X.-D. Yi, P.-P. Xu, C.-L. Tang, H.-L. Wan, K.-R. Tsai, T. Ikariya, Chirality 12 (2000) 383.
[85] J.-S. Chen, Y.-Y. Li, Z.-R. Dong, B.-Z. Li, J.-X. Gao, Tetrahedron Lett. 45 (2004) 8415.
[86] Z.-R. Dong, Y.-Y. Li, J.-S. Chen, B.-Z. Li, Y. Xing, J.-X. Gao, Org. Lett. 7 (2005) 1043.
[87] M.A. Bennet, A.K. Smith, J. Chem. Soc., Dalton Trans. (1974) 233.
[88] M.A. Bennet, T.N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 7 (1982) 74.
[89] R.A. Zelonka, M.C. Baird, J. Organomet. Chem. 35 (1972) C43.
[90] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.