Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 5395–5402
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and structural characterization of ruthenium(II) complexes bearing phosphine-pyrazolyl based tripod ligands

Weiqiang Tan, Xiaodan Zhao, Zhengkun Yu *

Dalian Institute of Chemical Physics, Chinese Academy of Sciences (CAS), 457 Zhongshan Road, Dalian, Liaoning 116023, PR China

Received 16 May 2007; received in revised form 17 August 2007; accepted 23 August 2007
Available online 29 August 2007

Abstract

Phosphine-pyrazolyl based tripod ligands $ROCH_2C(CH_2Pz)_2(CH_2PPh_2)$ (R = H, Me, allyl; Pz = pyrazol-1-yl) were efficiently synthesized and characterized. Reactions of these ligands with $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ afforded complexes of the type $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2](\mathbf{L})$ (**6**–**8**) in which the ligands exhibit κ^1-*P*-coordination to the metal center. Complex $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2\{Ph_2PCH_2C(CH_2OH)(CH_2Pz)_2\}]$ (**6**) underwent chloride-dissociation in CH_2Cl_2/MeCN to give complex $[RuCl(\eta^6\text{-}p\text{-cymene})\{\kappa^2(P,N)\text{-}Ph_2PCH_2C(CH_2OH)(CH_2Pz)_2\}][Cl]$ (**9**). Complexes **6**–**9** demonstrated poor to moderate catalytic activity in the transfer hydrogenation of acetophenone. All these complexes were fully characterized by analytical and spectroscopic methods and their molecular structures were determined by X-ray crystallographic study.

Keywords: Tripod ligands; Pyrazolyl; Phosphine; Ruthenium(II); *p*-Cymene

1. Introduction

Synthesis of neopentane-based tripod ligands has attracted considerable attention due to their interesting structural backbone, the ease of synthesis and potential applications in homogeneous catalysis [1]. A tripod ligand was usually constructed as $RC(CH_2PPh_2)_3$ in which three PPh_2 groups are linked to a neopentane backbone and such a ligand can be applied to prepare transition-metal catalysts for organic transformations [2]. Recently, Huttner et al. reported tripod ligands of type $RC(CH_2X)(CH_2Y)(CH_2Z)$ by introduction of different donor atoms to the neopentane backone [3]. In Huttner's tripod ligands at least one pyrazolyl donor group is employed to coordinate transition metals such as Mo [4a], Ni and Pd [4b,4c]. Transition-metal complexes bearing hemilabile P–N donor ligands have been extensively investigated [5]. It has been well known that phosphorus is a "soft" donor atom and nitrogen is a "hard" donor atom in an organic ligand. When both P and N are coordinated to the same metal center, the newly formed complexes usually exhibit catalytic activity to organic reactions [6]. Arene-ruthenium(II) complexes including those containing hemilabile P–N ligands [7] have been well studied and proved to be efficient pre-catalysts for a lot of organic reactions such as catalytic transfer hydrogenation of ketones [8].

During our ongoing investigation on pyrazolyl-based ligands, we have found that transition-metal complexes of polypyrazolyl ligands or mixed pyrazolyl-other donor ligands can work as excellent catalysts for organic reactions [9]. Keeping in mind the potential applications of tripod ligands, the mixed-donor tripod ligands with P, N and O donor atoms can be considered as a new class of ligands to construct Ru(II) complexes. To the best of our knowledge, phosphine-pyrazolyl tripod ligand-based Ru(II) complexes have not yet been reported. Herein, we report synthesis and structural characterization of (η^6-*p*-cymene)ruthenium(II) complexes with neopentane-type tripod ligands bearing P, N and O donor atoms. The complexes were preliminarily tested as catalysts for catalytic transfer hydrogenation of acetophenone.

* Corresponding author. Tel./fax: +86 411 8437 9227.
E-mail address: zkyu@dicp.ac.cn (Z. Yu).

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.08.025

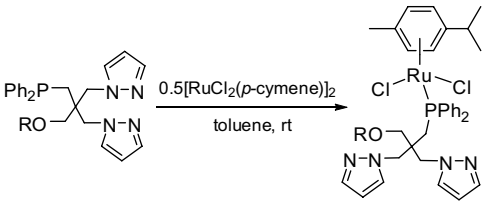
2. Results and discussion

2.1. Synthesis of ligands 4, 5a and 5b

The tripod ligand **4** was synthesized in four steps by a modified known procedure [4a] (Chart 1). Tribromide **1** was prepared in 68% yield from the reaction of pentaerythritol with 40% aqueous HBr solution in acetic acid [10]. Using a modified literature procedure, the ring closure reaction to form dibromide **2** successfully proceeded in the presence of sodium ethoxide, affording **2** in 62% yield [11]. Treatment of **2** with >2.0 equiv. potassium pyrazolate generated from the reaction of pyrazole and KO^{t}Bu in THF afforded the bis(pyrazolyl) derivative **3**. Nucleophilic cleavage of the oxetane ring in **3** with $LiPPh_2$ in THF resulted in CH_2OH-functionalized tripod ligand **4** [4a]. In order to adjust the coordination capability of tripod ligand **4**, the CH_2OH group in its backbone was alkylated into the corresponding methyl and allyl ethers with methyl iodide and allyl bromide in the presence of a base, respectively [4a]. The ^1H and ^{13}C NMR spectroscopies are in agreement with the proposed structures of ligands **4**, **5a** and **5b**, and their $^{31}P\{^1H\}$ NMR signals are shown in the region of −27.2 to −26.7 ppm, typical of phosphine ligands.

2.2. Synthesis of complexes 6–8

Treatment of $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ with 2.0 equiv. of **4**, **5a** or **5b** in toluene at ambient temperature gave the product **6**, **7** or **8** as a red solid in high yields (81–98%) (Eq. (1)). These complexes are air- and moisture-stable at ambient temperature and the spectroscopic and elemental analyses are consistent with the suggested molecular formulae of complexes **6**–**8** and their molecular structures were further confirmed by X-ray crystallographic determinations



(1)

4, **5a** or **5b** R =: H (**6**); Me (**7**); allyl (**8**)

Complexes **6**–**8** demonstrate very similar NMR features in solution. The ^1H and ^{13}C NMR spectra of complexes **6**–**8** reveal the presence of *p*-cymene and ligand **4**, **5a** or **5b** in a 1:1 molar ratio in a complex molecule. Their ^{31}P NMR signals appear at 14.6–16.1 ppm, suggesting that the phosphorus atom in the ligands is coordinated to the metal center in the complexes [12] as compared to those of the free ligands ($\delta(^{31}P)$: −27.2 to −26.7 ppm). In the proton NMR spectra of the complexes, the ^1H NMR signals of the pyrazolyl NCH moieties are present as two coalesced doublets in the region 8.01–7.84 ppm, while these signals are separate from 0.03 to 0.23 ppm in the proton NMR spectra of the free ligands, and those of the pyrazolyl CH groups are shown as a triplet at *ca.* 6.20 ppm. The resonance signals of the NCH_2 moieties are split into two doublets in the region of 4.07–3.65 ppm, while the PCH_2 group presents one doublet at 2.98–3.25 ppm. The proton NMR signals of *p*-cymene appear in the region 5.29–4.99 ppm as two doublets for the aromatic CH moieties, at *ca.* 2.48 ppm as multiple peaks for the CH group of the isopropyl, *ca.* 1.78 ppm as a singlet for the methyl, and 0.70–0.91 ppm as a doublet for the two methyls of the isopropyl. Based on these results, it is clear that the two pyrazolyl moieties are not chemically equivalent and situated in an unsymmetrical environment. The oxygen atom in complex **7** and the vinyl moiety in complex **8** are not coordinated to the metal center because the proton NMR signals of the corresponding OCH_3 and $-CH{=}CH_2$ moieties almost

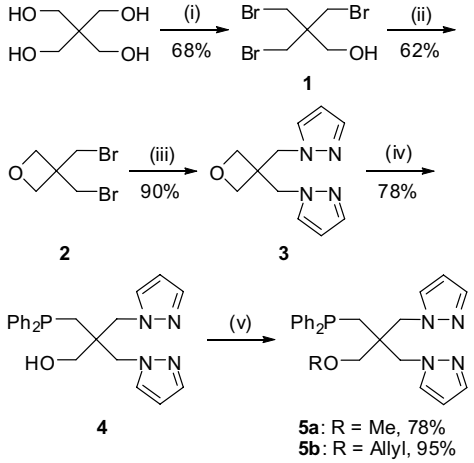


Chart 1. Synthesis of tripod ligands **4**, **5a** and **5b**. Conditions: (i) 40% HBr, HOAc, H_2SO_4, 160 °C, 24 h; (ii) NaOEt, EtOH, reflux, 3 h; (iii) pyrazole, KO^{t}Bu, THF, reflux, 12 h; (iv) $HPPh_2$, ^{n}BuLi, THF, 23 °C, 10 h; (v) for **5a**: MeI, KO^{t}Bu, THF, 23 °C, 3 h; for **5b**: allyl bromide, NaH, THF, 23 °C, 12 h.

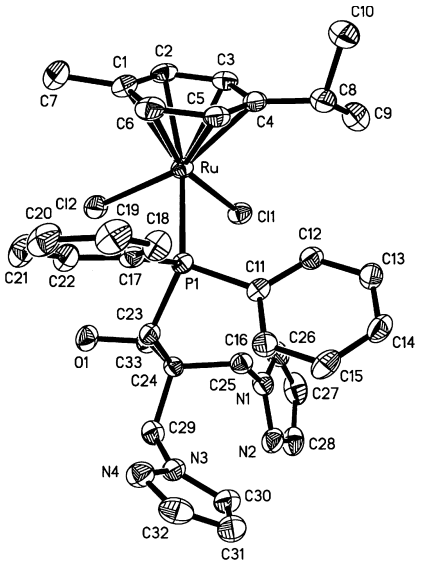
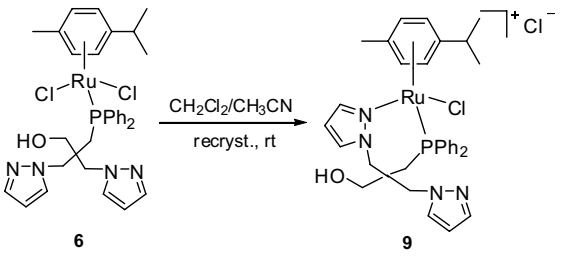


Fig. 1. Perspective view of complex **6**.

appear at the same positions as those of the free ligands **5a** and **5b**, respectively. It should be noted that the proton NMR signal of the $HOCH_2$ group in complex **6** is shifted 0.18 ppm upfield as compared to that of the free ligand **4** due to formation of an intramolecular hydrogen bond between the hydroxy hydrogen of the $HOCH_2$ group and one of the chloride atoms (see the X-ray crystallographic studies). The broad stretching vibration of O–H (ν 3436 cm^{-1}) further reveals presence of a hydrogen bond in **6**. It is presumably attributed to the sterical and electronic requirements of such a tripod ligand that prevents compounds **4**, **5a** and **5b** from acting as polydentate ligands in the complexes



(2)

2.3. Formation of complex 9

Complexes **6**–**8** were synthesized in decent yields and further purified by recrystallization. Unexpectedly, recrystallization of powdered complex **6** in CH_2Cl_2/CH_3CN at −20 °C only afforded complex **6** as red crystals in 58% yield. After concentrated under reduced pressure, the mother liquor from the recrystallization was layered by *n*-hexane and kept in an air atmosphere at ambient temperature overnight, giving complex **9** as orange crystals in 38% yield (Eq. (2)). Complex **9** is a cationic complex without coordinating solvent as its ligand(s). The NMR spectra of **9** exhibit obvious difference from those of its corresponding neutral complex **6**, that is, the proton NMR signals of the pyrazolyl NCH and CH, aromatic CH of *p*-cymene, NCH_2, $HOCH_2$ and PCH_2 moieties in **9** are shifted downfield, respectively, while those of the methyl and *iso*-propyl groups of the *p*-cymene group are shifted upfield and showed as two doublets for the two methyl groups of the *iso*-propyl. The ^{31}P NMR signal of **9** appears at 17.00 ppm, shifting downfield as compared to that of its corresponding neutral complex **6**. The broad stretching vibration of O–H (ν 3426 cm^{-1}) reveals presence of a hydrogen bond in **9**

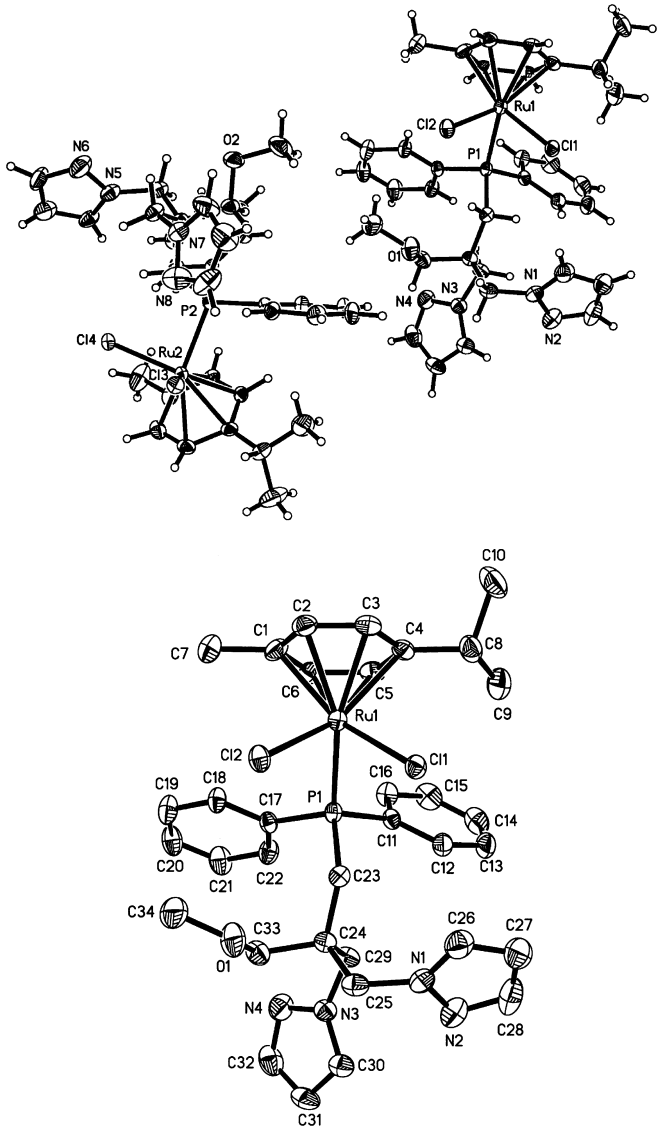


Fig. 2. Perspective view of complex **7**.

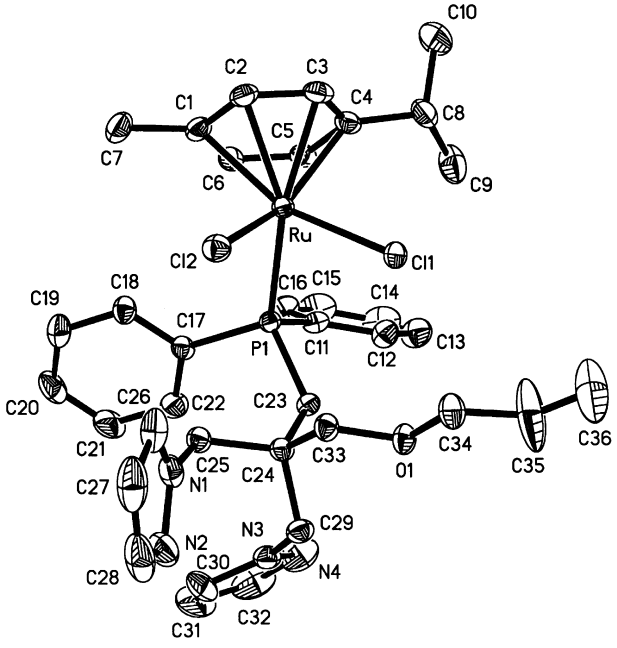


Fig. 3. Perspective view of complex **8**.

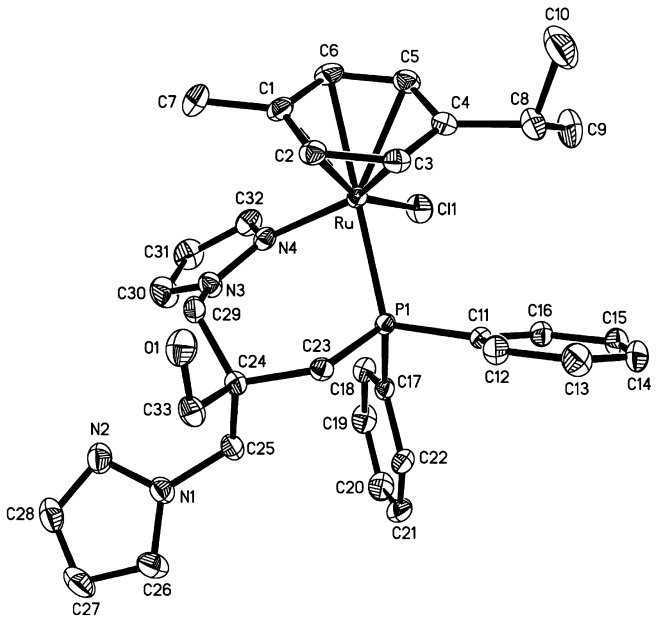
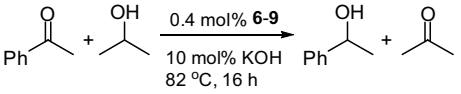


Fig. 4. Perspective view of complex **9**.



(3)

2.4. Catalytic transfer hydrogenation of acetophenone

The catalytic activity of complexes **6–9** was tested in the transfer hydrogenation of acetophenone in 2-propanol (Eq. (3)). The catalytic reaction was carried out on a scale of 2 mmol acetophenone with 0.4 mol% of the complexes as catalyst in the presence of KOH at 82 °C. Over a period of 16 h, the corresponding alcohol was formed as the only product by GC analysis (Table 3). Using complex **6** and **9** as catalyst, the alcohol product was formed in 68% and 54% yields, respectively, while less than 10% of the product was produced using complex **7** or **8** as catalyst. These results reveal that complexes **6–9** are poorer catalysts for transfer hydrogenation of acetophenone under the stated conditions than $[RuCl_2(p\text{-cymene})]_2$ [8d,13]. The hydroxyl group in complexes **6** and **9** is presumably involved in formation of the catalytically active species, which is attributed to the much higher catalytic activity of complexes **6** and **9** than **7** and **8**. Presence of a hydrogen bond O–H···Cl in **6** and **9** may promote such an involvement.

2.5. X-ray crystal structures of complexes 6–9

The solid-state single crystal structures of complexes **6–9** were determined by X-ray crystallographic study and their molecular structures are shown in Figs. 1–4. The crystallographic data for these complexes is summarized in Table 1, and selected bond lengths and angles are

Table 1
Crystal data and refinement details for compounds **6**, **7a**, **7b** and **8**

	6	**7**	**8** · $0.5CH_2Cl_2$	**9**
Empirical formula	$C_{33}H_{39}N_4OCl_2PRu$	$C_{34}H_{41}N_4OCl_2PRu$	$C_{37}H_{44}N_4OCl_3PRu$	$C_{33}H_{39}N_4OCl_2PRu$
Formula weight	710.62	724.65	799.15	710.62
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$
a (Å)	9.355(2)	10.2903(6)	10.6074(16)	15.0586(8)
b (Å)	19.797(4)	17.3622(11)	11.1412(17)	10.0914(5)
c (Å)	17.565(4)	18.8370(11)	16.493(3)	21.0404(11)
α (°)	90	91.9480(10)	104.992(3)	90
β (°)	98.838(4)	92.2170(10)	91.644(3)	95.5670(10)
γ (°)	90	91.7630(10)	98.865(3)	90
V (Å^3)	3214.4(12)	3359.3(3)	1855.5(5)	3182.3(3)
Z	4	4	2	4
D_{calc} (g cm^{-3})	1.468	1.433	1.430	1.483
μ (mm^{-1})	0.737	0.707	0.717	0.744
$F(000)$	1464	1496	824	1464
Crystal size (mm)	$0.25 \times 0.15 \times 0.12$	$0.52 \times 0.49 \times 0.18$	$0.42 \times 0.39 \times 0.31$	$0.52 \times 0.44 \times 0.43$
θ Limits (°)	1.56–27.00	1.08–27.00	1.92–27.00	1.59–27.00
Number of data collected	18384	19885	11033	18185
Number of unique data	6895	14238	7889	6888
R_{int}	0.1200	0.0495	0.0568	0.0592
Number of data observed with $I > 2\sigma(I)$	3822	9630	6639	6039
Number of refined parameters	383	783	422	386
Goodness-of-fit on F^2	0.834	0.923	0.994	1.029
R (observed data/all data)	0.0948/0.0523	0.0460/0.0706	0.0446/0.0519	0.0331/0.0383
wR^2 (observed data/all data)	0.1050/0.1149	0.0952/0.1076	0.1148/0.1190	0.0820/0.0844
Residual ρ_{max} (e Å^{-3})	1.547 (−0.510)	1.016 (−0.561)	1.093 (−0.826)	0.671 (−0.499)

Table 2
Selected bond lengths (Å) and angles (°) for compounds **6–9**

Complex ***6***					
Ru–P(1)	2.3647(12)	O(1)–C(33)	1.418(5)		
Cl(1)–Ru–Cl(2)	88.26(5)	P(1)–Ru–Cl(1)	89.34(4)		
P(1)–Ru–Cl(2)	85.49(4)	Ru–P(1)–C(23)	124.89(15)	O(1)–H(1)···Cl(2)	2.43
Complex 7					
Ru(1)–P(1)	2.3714(10)	O(1)–C(33)	1.420(5)	O(1)–C(34)	1.409(5)
Ru(2)–P(2)	2.3681(10)				
Cl(1)–Ru(1)–Cl(2)	87.59(4)	P(1)–Ru(1)–Cl(1)	86.05(4)		
P(1)–Ru(1)–Cl(2)	88.09(4)	Ru–P(1)–C(23)	110.37(12)		
Ru(2)–P(2)–C(57)	112.40(12)				
Complex ***8***					
Ru–P(1)	2.3693(8)	O(1)–C(33)	1.420(4)	O(1)–C(34)	1.414(4)
Cl(1)–Ru–Cl(2)	89.85(3)	P(1)–Ru–Cl(1)	84.15(3)	P(1)–Ru–Cl(2)	88.81(3)
Ru–P(1)–C(23)	111.30(7)				
Complex ***9***					
Ru–P(1)	2.3398(6)	O(1)–C(33)	1.411(3)	Ru(1)–N(4)	2.1080(18)
O(1)–H(1)···Cl(2)	2.148(18)				
N(4)–Ru–P(1)	85.05(5)	N(4)–Ru–Cl(1)	88.43(5)	P(1)–Ru–Cl(1)	88.27(2)

Table 3
Catalytic transfer hydrogenation of acetophenone[a]

Entry	Catalyst	Time (h)	Yield (%)
1	**6**	16	68
2	**7**	16	<10
3	**8**	16	<10
4	**9**	16	54

[a] Conditions: acetophenone (2.0 mmol); ketone/catalyst/KOH = 250:1:17; 2-propanol (10 ml); 0.1 MPa, 82 °C. Yields determined by GC analysis.

listed in Table 2. Complexes **6–8** exhibit similar molecular structures which are constructed with a [$RuCl_2$(*p*-cymene)] unit and a tripod ligand. The metal center is coordinated by an η^6-*p*-cymene moiety and a tripod ligand through its phosphorus atom. The Ru(1)–P(1) bond distances in **6–8** are 2.3647(12), 2.3714(10) and 2.3693(8) Å, respectively and the Ru(1)–P(1)–C(23) angles range from 110.37(12)° to 124.89(15)° (Table 2). The oxygen and pyrazolyl nitrogen atoms, and/or the vinyl moiety are not coordinated to the ruthenium atom, that is, tripod ligands **4**, **5a** and **5b** act as monodentate ligands in the complexes. It should be noted that there exists a hydrogen bond in complex **6** (O(1)–H(1)···Cl(2), 2.43 Å) and two independent molecules of complex **7** are present in an asymmetric unit with Ru(2)–P(2) bond distance of 2.3681(10) Å and Ru(2)–P(2)–C(57) angle of 112.40(12)° (Fig. 2). In complex **9**, the tripod ligand **4** acts as a bidentate ligand with one of its pyrazolyl nitrogen atoms and the phosphorus atom coordinating to the metal center, forming a seven-membered metal-containing P,N-heterocycle. The Ru–N bond distance (2.1080(18) Å) in **9** is in accordance with those reported for Ru–N complexes [14]. There also exists a hydrogen bond in complex **9** (O(1)–H(1)···Cl(2), 2.15 Å).

3. Summary

In summary, phosphine-pyrazolyl based tripod ligands were synthesized and applied to construct a new type of complexes [Ru(η^6-*p*-cymene)Cl_2](**L**) in which the ligands exhibit κ^1-*P*-coordination to the metal center. Complex [Ru(η^6-*p*-cymene)Cl_2{$Ph_2PCH_2C(CH_2OH)(CH_2Pz)_2$}] underwent chloride-dissociation in a polar solvent to form cationic complex [RuCl(η^6-*p*-cymene){κ^2(*P*,*N*)-$Ph_2PCH_2C(CH_2OH)(CH_2Pz)_2$}][Cl]. Complexes **6–9** have demonstrated potential catalytic activity for organic reactions.

4. Experimental

4.1. General considerations

All the reactions were carried out under a nitrogen atmosphere with a drybox and standard Schlenk techniques. Chemicals were used as received. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a 400 MHz spectrometer and chemical shift values refer to $\delta_{TMS} = 0.00$ ppm or $CDCl_3$ ($\delta(^1H)$, 7.26 ppm; $\delta(^{13}C)$, 77.16 ppm) and H_3PO_4 (85%). IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer. High resolution mass spectra (HRMS) was recorded on a Mariner 5300 HPLC-MS spectrometer. 3-Bromo-2,2-bis(bromomethyl)-propan-1-ol (**1**) [10], 3-(diphenylphosphanyl)-2,2-bis(pyrazol-1-yl-methyl)-propan-1-ol (**4**) [4a], 3-(diphenylphosphanyl)-2,2-bis(pyrazol-1-ylmethyl) propyl methyl ether (**5a**) [4a], and [$RuCl_2$(*p*-cymene)]$_2$ [15] were prepared as reported. 3,3-Bis(bromomethyl)oxetane (**2**) [10] and 3,3-bis(pyrazol-1-ylmethyl)oxetane (**3**) [4a] were synthesized by modified literature methods, respectively. The NMR spectra of the known compounds were obtained and are in accord with their reported spectra.

4.2. Synthesis of the ligands

4.2.1. Synthesis of 3,3-bis(bromomethyl)oxetane (**2**) [10]

A mixture of pentaerythritol (12.80 g, 94.0 mmol) in 60 ml of glacial HOAc and 40% aqueous HBr (v/v, 1/5) was refluxed for 24 h, and then 50 ml 40% aqueous HBr and 23 ml 98% sulfuric acid were added. The resulting solution was further refluxed for 24 h. After cooling to the ambient temperature, the mixture was separated and the product phase was diluted with 50 ml $CHCl_3$, washed with water (2×20 ml), and dried over anhydrous potassium carbonate, and then filtered. All the volatiles were removed under reduced pressure. The resultant residue was distilled under reduced pressure to afford tribromide **1** as a colorless liquid (21.50 g, 68%; b.p.: 130–135 °C/0.3 mmHg). An ethanolic solution of sodium ethoxide (1.1 M, 100 ml) was added to a mixture of **1** (37.00 g, 0.11 mol) and 150 ml ethanol and the resulting mixture was stirred at 80 °C for 2.5 h, and then cooled to ambient temperature and filtered. All the volatiles were removed under reduced pressure to afford a viscous residue which was distilled in vacuum, giving dibromide **2** (16.70 g, 62%; b.p.: 62–64 °C/0.3 mmHg).

4.2.2. Synthesis of 3,3-bis(pyrazol-1-yl-methyl)oxetane (**3**) [4a]

A solution of dibromide **2** (4.14 g, 16.9 mmol) in 30 ml THF was added to a mixture of potassium pyrazolate freshly prepared from the reaction of KO^tBu (3.18 g, 37.3 mmol) and pyrazole (2.50 g, 37.3 mmol) in 30 ml THF at 0 °C over a period of 20 min. After warmed to ambient temperature, the mixture was refluxed with stirring for 12 h, and then cooled, filtered through Celite. The filtrate was concentrated under reduced pressure. The resultant residue was purified by flash silica gel column chromatography with petroleum ether (60–90 °C)/diethyl ether (v/v, 1:1) as the eluent, affording compound **3** as a colorless oil (3.34 g, 90%).

4.2.3. Synthesis of 3-(diphenylphosphanyl)-2,2-bis(pyrazol-1-ylmethyl)propyl allyl ether (**5b**)

To a solution of **4** (0.30 g, 0.74 mmol) in 10 ml THF was added NaH (0.03 g, 1.11 mmol) at 0 °C with stirring. After gas evolution ceased, allyl bromide (0.14 g, 1.11 mmol) in 5 ml of THF was added. The mixture was stirred at ambient temperature for 12 h, filtered through Celite and concentrated under reduced pressure. The resulting viscous oil was purified by silica gel column chromatography using petroleum ether (60–90 °C)/diethyl ether (v/v, 4/1) as the eluent to give **5b** as a colorless liquid (0.31 g, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz, 23 °C) δ 7.78 and 7.64 (br each, 2:2H, CHN of Pz), 7.42 and 7.28 (m each, 4:6H, $2 \times$ Ph), 6.24 (br, 2H, CH of Pz), 5.69 (m, 1H, CH of allyl), 5.15 and 5.11 (d each, 1:1H, CH_2 of allyl), 4.37 (dd, 2:2H, NCH_2), 3.50 (d, 2H, OCH_2–CH=CH_2), 3.05 (s, 2H, OCH_2), 2.23 (s, 2H, PCH_2); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 139.39 (s, N=CH of Pz), 139.12 and 139.01 (s, Cq, *i*-C of $2 \times$ Ph), 134.43, 133.18, 132.98, 131.86, 128.64, 128.50 and 128.44 and 116.79 (CH of Pz, $2 \times$ Ph, allyl), 105.18 (s, CH of Pz), 71.69, 71.58 and 71.49 (s each, 1:1:1, =CH_2, $2 \times OCH_2$), 54.53 and 45.22 (d each, NCH_2), 31.52 (d, PCH_2); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −26.75; HRMS (APCI) calcd for $C_{26}H_{30}N_4OP$ ($M+H^+$): 445.2157, found: 445.2118.

4.3. Synthesis of the complexes **6**–**8**

4.3.1. Synthesis of [Ru(η^6-*p*-cymene)Cl_2\{κ^1(*P*)-$PPh_2CH_2C(CH_2OH)(CH_2Pz)_2$\}] (**6**)

A mixture of [$RuCl_2$(*p*-cymene)]$_2$ (76 mg, 0.12 mmol) and **4** (100 mg, 0.24 mmol) in 20 ml toluene was stirred at ambient temperature for 5 h, forming red-orange precipitate. All the volatiles were removed under reduced pressure and the resultant residue was washed with diethyl ether (3×10 ml) and dried in vacuo to afford complex **6** as a dark red microcrystalline power (172 mg, 98%). M.p.: 165 °C, dec. Single crystals suitable for X-ray crystallographic determination were grown from recrystallization in pentane/CH_2Cl_2 (v/v, 3/1). ^{1}H NMR ($CDCl_3$, 400 MHz, 23 °C) δ 7.87 and 7.85 (dd, 2:2H, NCH of Pz), 7.69 and 7.46 (m each, 2:8H, $2 \times$ Ph), 6.23 (t, 2H, CH of Pz), 5.14 and 4.99 (d each, 2:2H, aromatic CH of *p*-cymene), 3.69 (dd, 2:2H, NCH_2), 3.05 (s, 2H, OCH_2), 2.99 (d, 2H, PCH_2), 2.49 (m, 1H, CH of ^{i}Pr), 1.79 (s, 3H, Me), 0.89 (d, 6H, $2 \times$ Me of ^{i}Pr); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 139.23 (s, N=CH), 134.22 and 133.82 (Cq, *i*-C of $2 \times$ Ph), 133.24, 133.15, 132.50, 131.28, 128.79, 128.69, 109.64, 105.49, 94.62, 90.52, 85.69, 85.64, 63.24, 54.68 (d), 47.15, 30.15, 27.49 (d) 21.70, 17.45; ^{31}P{^{1}H} NMR ($CDCl_3$) δ 16.08 ppm; IR (KBr) cm^{-1} ν(O–H) 3436 (br). Anal. Calc. for $C_{33}H_{39}Cl_2N_4OPRu \cdot 0.33CH_2Cl_2$: C, 54.18; H, 5.41; N, 7.58. Found: C, 54.33; H, 5.61; N, 7.49%.

4.3.2. Synthesis of [Ru(η^6-*p*-cymene)Cl_2\{κ^1(*P*)-$PPh_2CH_2C(CH_2OMe)(CH_2Pz)_2$\}] (*R* = *Me* (**7**); *allyl* (**8**))

In a fashion similar to synthesis of complex **6**, treatment of [$RuCl_2$(*p*-cymene)]$_2$ with 2.0 equiv. of ligand **5a** or **5b** in toluene afforded complex **7** or **8** as the product.

4.3.2.1. Synthesis of complex 7. A mixture of [$RuCl_2$(*p*-cymene)]$_2$ (256 mg, 0.418 mmol) and **5a** (350 mg, 0.836 mmol) in 20 ml toluene was stirred at ambient temperature for 6 h afforded complex **7** (480 mg, 81%). Orange crystals of **7** were obtained by recrystallization from dichloromethane/hexane (v/v, 1/3) at −20 °C. M.p.: 167 °C, dec. ^{1}H NMR ($CDCl_3$, 400 MHz, 23 °C) δ 7.97 (br, 4 H), 7.64 and 7.43 (br and m each, 2:8H, $2 \times$ Ph), 6.20 (br, 2H, CH of Pz), 5.14 and 4.98 (d each, 2:2H, CH of *p*-cymene), 3.90 (dd, 2:2H, $2 \times NCH_2$), 3.14 (d, 2H, PCH_2), 2.80 (s, 3H, OCH_3), 2.57 (s, 2H, OCH_2), 2.43 (m, 1H, CH of ^{i}Pr), 1.74 (s, 3H, CH_3), 0.67 (d, 6H, $2 \times$ Me of ^{i}Pr); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 139.13 (s, N=CH), 134.34 and 133.94 (Cq, *i*-C of $2 \times$ Ph), 133.31, 133.22, 132.34, 130.85, 128.42, 128.32, 109.11, 105.31, 94.31, 90.66, 85.29, 72.69,

58.08, 54.61, 45.95 (d), 30.03, 27.43 (d), 21.68, 17.24; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 14.91 ppm; IR (KBr) cm^{-1} $\nu(OCH_3)$ 2922 (C–O–C) 1093. Anal. Calc. for $C_{34}H_{41}Cl_2N_4OPRu$: C, 56.35; H, 5.70; N, 7.73. Found: C, 56.15; H, 5.86; N, 7.57%.

*4.3.2.2. Synthesis of complex **8**.* A mixture of $[RuCl_2(p\text{-cymene})]_2$ (284 mg, 0.463 mmol) and **5b** (412 mg, 0.927 mmol) in 20 ml toluene was stirred at ambient temperature for 12 h afforded complex **8** (611 mg, 89%). Dark red crystals were obtained by recrystallization from dichloromethane/*n*-hexane (v/v, 1/3) at −20 °C. M.p.: 162 °C, dec. ^1H NMR ($CDCl_3$, 400 MHz, 23 °C) δ 8.00 and 7.98 (d each, 2:2H, 2 × NCH of Pz), 7.69 and 7.46 (m each, 2:8H, 2 × Ph), 6.22 (t, 2H, CH of Pz), 5.72 (m, 1H, CH of allyl), 5.17 and 5.03 (d each, 2:2H, 4H, aromatic CH of *p*-cymene), 5.10 (m, 2H, CH_2 of allyl), 3.98 (dd, 2:2H, 4H, 2 × NCH_2), 3.46 and 3.23 (d each, 2:2H, 2 × OCH_2), 2.67 (s, 2H, PCH_2), 2.48 (m, 1H, CH of ^{i}Pr), 1.77 (s, 3H, CH_3), 0.91 (d, 6H, 2 × Me of ^{i}Pr); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 139.11 (s, Cq, N=CH), 134.56, 134.39, 133.98, 133.42, 133.34, 132.34, 130.84, 128.41, 128.32, 116.63, 109.28, 105.31, 94.51, 90.59, 85.34 (d), 71.66, 70.74, 46.06, 30.05, 27.99, 21.70, 17.22; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 23 °C) δ 14.72 ppm; IR (KBr) cm^{-1} $\nu(CH_2CH{=}CH_2)$ 3040, 2964. Anal. Calc. for $C_{36}H_{43}Cl_2N_4OPRu \cdot 0.5CH_2Cl_2$: C, 55.61; H, 5.55; N, 7.01. Found: C, 55.37; H, 5.70; N, 6.89%.

*4.3.3. Synthesis of $[Ru(\eta^6\text{-}p\text{-cymene})Cl\{\kappa^2(P,N)\text{-}PPh_2CH_2C(CH_2OH)(CH_2Pz)_2\}][Cl]$ (**9**)*

Recrystallization of powdered complex **6** (860 mg, 1.21 mmol) in CH_2Cl_2/MeCN (v/v, 3/1) at −20 °C overnight afforded **6** as red crystals (508 mg, 58%). The mother liquor from the recrystallization was concentrated under reduced pressure, layered by *n*-hexane and kept in an air atmosphere at ambient temperature overnight, giving complex **9** as orange crystals (333 mg, 38%). M.p. 210 °C, dec. ^1H NMR ($CDCl_3$, 400 MHz, 23 °C) δ 8.95 and 8.53 (d each, 1:1H, NCH of coordination Pz), 7.48 and 7.45 (d each, 1:1H, NCH of uncoordinated Pz), 7.49, 7.21, 7.04 and 6.63 (m each, 10H, 2 × Ph), 6.63 (t, 1H, CH of coordinated Pz), 6.16 (t, 1H, CH of uncoordinated Pz), 6.07 and 5.89 (m each, 4H, aromatic CH of *p*-cymene), 4.79 (dd, 1H, CH_2N-coordinated Pz), 4.69 (q, 2H, CH_2N-uncoordinated Pz), 3.57 (d, 1H, CH_2N-coordinated Pz), 3.01 (s, 2H, CH_2OH), 2.95 (m each, 2H, PCH_2), 1.75 (m, 1H, CH of ^{i}Pr), 1.43 (s, 3H, CH_3), 1.06 and 0.83 (d each, 3:3H, 2 × CH_3 of ^{i}Pr); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 23 °C) δ 149.68, 141.24, and 139.92 (1:1:2, NCH of Pz), 136.75 and 136.27 (Cq, *i*-C of 2 × Ph), 134.22, 134.13, 132.69, 131.80, 131.19, 129.53, 129.44, 128.22 and 128.12 (aromatic CH of 2 × Ph and *p*-cymene), 109.40, 105.51, 103.00, 91.44, 90.34, 89.52, 65.14, 54.53 and 52.56 (2 × NCH_2), 45.23 (PCH_2), 36.41 (br, Cq), 30.48 (CH of ^{i}Pr), 23.21 and 21.71 (2 × Me of ^{i}Pr), 17.48 (Me); $^{31}P\{^1H\}$ NMR (DMSO-d_6) δ 16.97 ppm; IR (KBr) cm^{-1} ν(O–H) 3425 (br); Anal. Calc. for $C_{33}H_{39}Cl_2N_4OPRu$: C, 55.77; H, 5.53; N, 7.88. Found: C, 55.76; H, 5.67; N, 7.79%.

4.4. Transfer hydrogenation of acetophenone

Under nitrogen atmosphere, acetophenone (2.0 mmol), the catalyst (0.008 mmol) and 15 ml of a 0.10 M solution of KOH in 2-propanol, were subsequently loaded into a 50 ml Schlenk flask equipped with a condenser and a magnetic bar. The mixture was stirred at 82 °C and the reaction was monitored by GC analysis.

4.5. X-ray crystallographic studies

Single crystal X-ray diffraction studies for complex **6**–**9** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). 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 structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. Crystal data and refinement details for these complexes are summarized in Table 1.

Acknowledgements

We are grateful to the "Hundred Talented Program" Funding of CAS and the National Natural Science Foundation of China (Grant No. 20501018) for support of this research.

Appendix A. Supplementary material

CCDC 647042, 647041, 647039 and 647040 contains the supplementary crystallographic data for **6**, **7**, **8** and **9**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.025.

References

[1] (a) H.A. Mayer, W.C. Kaska, Chem. Rev. 94 (1994) 1239;
(b) C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, F. Zanobini, Coord. Chem. Rev. 120 (1992) 193.
[2] (a) C. Bianchini, A. Meli, A. Orlandini, L. Sacconi, J. Organomet. Chem. 209 (1981) 219;
(b) C. Bianchini, D. Masi, A. Meli, M. Peruzzini, J. Am. Chem. Soc. 110 (1988) 6411;
(c) C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, Organometallic 9 (1990) 226.

[3] Selected recent papers, see: (a) R. Soltek, G. Huttner, Eur. J. Inorg. Chem. 10 (1998) 1417;
(b) B. Antelmann, U. Winterhalter, G. Huttner, B.C. Janssen, J. Organomet. Chem. 545–546 (1998) 407;
(c) B. Antelmann, G. Huttner, U. Winterhalter, J. Organomet. Chem. 553 (1998) 433;
(d) J. Vogelgesang, G. Huttner, E. Kaifer, P. Kircher, P. Rutsch, S. Cunskis, Eur. J. Inorg. Chem. 12 (1999) 2187;
(e) J. Vogelgesang, A. Frick, G. Huttner, P. Kircher, Eur. J. Inorg. Chem. 4 (2001) 949.

[4] (a) A. Jacobi, G. Huttner, U. Winterhalter, S. Cunskis, Eur. J. Inorg. Chem. 6 (1998) 675;
(b) R. Faissner, G. Huttner, E. Kaifer, P. Rutsch, Eur. J. Inorg. Chem. 9 (2003) 1681;
(c) R. Faissner, G. Huttner, E. Kaifer, P. Kircher, L. Zsolnai, P. Rutsch, L. Zsolnai, Eur. J. Inorg. Chem. 12 (2003) 2219.

[5] For reviews on hemilabile ligands, see: (a) A. Bader, E. Linder, Coord. Chem. Rev. 108 (1991) 27;
(b) E. Lindner, S. Pautz, M. Haustein, Coord. Chem. Rev. 155 (1996) 145;
(c) P. Braunstein, F. Naud, Angew. Chem., Int. Ed. 40 (2001) 680;
(d) P. Braunstein, J. Organomet. Chem. 689 (2004) 3953.

[6] Selected recent papers, see: (a) C. Dubs, T. Yamamoto, A. Inagaki, M. Akita, Organometallics 25 (2006) 1344;
(b) R. Tribó, S. Muńoz, J. Pons, R. Yáñez, A. Álvarez-Larena, J.F. Piniella, J. Ros, J. Organomet. Chem. 690 (2005) 4072;
(c) G. Esquius, J. Pons, R. Yánez, J. Ros, R. Mathieu, N. Lugan, B. Donnadieu, J. Organomet. Chem. 667 (2003) 126;
(d) B. Therrien, T.R. Ward, Angew. Chem., Int. Ed. 38 (1999) 405.

[7] (a) T. Naota, H. Takaya, S.-I. Murahashi, Chem. Rev. 98 (1998) 2599;
(b) B.M. Trost, F.D. Toste, A.B. Pinkerton, Chem. Rev. 101 (2001) 2067.

[8] (a) G. Zassinovich, G. Mestroni, S. Gladiali, Chem. Rev. 92 (1992) 1051;
(b) R. Noyori, S. Hashiguchi, Acc. Chem. Res. 30 (1997) 97;
(c) D. Carmona, M.P. Lamata, L.A. Oro, Eur. J. Inorg. Chem. 9 (2002) 2239;
(d) P. Crochet, M.A. Fernández-Zúmel, J. Gimeno, M. Scheele, Organometallics 25 (2006) 4846.

[9] (a) Z.K. Yu, F.L. Zeng, X.J. Sun, H.X. Deng, J.H. Dong, J.Z. Chen, H.M. Wang, C.X. Pei, J. Organomet. Chem. 692 (2007) 2306;
(b) F.L. Zeng, Z.K. Yu, J. Org. Chem. 71 (2006) 5274;
(c) H.X. Deng, Z.K. Yu, J.H. Dong, S.Z. Wu, Organometallics 24 (2005) 4110;
(d) X.J. Sun, Z.K. Yu, S.Z. Wu, W.-J. Xiao, Organometallics 24 (2005) 2959.

[10] C.G. Overberger, Y. Okamoto, V. Bulacovschi, Macromolecules 8 (1975) 31.

[11] C.H. Issidorides, R.C. Gulen, N.S. Aprahamian, J. Org. Chem. 21 (1956) 997.

[12] I. Moldes, E. de la Encarnación, J. Ros, Á. Alvarez-Larena, J.F. Piniella, J. Organomet. Chem. 566 (1998) 165.

[13] (a) A. Caballero, F.A. Jalon, B.R. Manzano, G. Espino, M. Perez-Manrique, A. Mucientes, F.J. Poblete, M. Maestro, Organometallics 23 (2004) 5694;
(b) P. Crochet, M.A. Fernandez-Zumel, C. Beauquis, J. Gimeno, Inorg. Chim. Acta 356 (2003) 114.

[14] (a) R.P. Schutte, S.J. Rettig, A.M. Joshi, B.R. James, Inorg. Chem. 36 (1997) 5809;
(b) G. Jia, H.M. Lee, I.D. Williams, C.P. Lau, Y. Chen, Organometallics 16 (1997) 3941;
(c) S.E. Durran, M.B. Smith, A.M.Z. Slawin, J.W. Steed, J. Chem. Soc., Dalton Trans. 16 (2000) 2771.

[15] M.A. Bennettt, A.K. Smith, J. Chem. Soc., Dalton Trans. 2 (1974) 233.