Syntheses of Ru–η^6-C$_6$H$_6$-diphosphine complexes and their catalytic properties for hydrogenation of benzene

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Abstract

Six Ru–η^6-C$_6$H$_6$-diphosphine complexes, [RuCl(η^6-C$_6$H$_6$)(BISBI)]Cl (**1**) (BISBI = 2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl), [RuCl-(η^6-C$_6$H$_6$)(BDPX)]Cl (**2**) (BDPX = 1,2-bis(diphenylphosphinomethyl)benzene), Ru$_2$Cl$_4$(η^6-C$_6$H$_6$)$_2$(μ$_2$-BDNA) (**3**) (BDNA = 1,8-bis(diphenyl-phosphinomethyl)naphthalene), [RuCl(η^6-C$_6$H$_6$)(BISBI)]BF$_4$ (**4**), [RuCl(η^6-C$_6$H$_6$)(BDPX)]BF$_4$ (**5**) and [(η^6-C$_6$H$_6$)$_2$Ru$_2$Cl$_2$(μ$_2$-Cl)(μ$_2$-BDNA)]BF$_4$ (**6**) were prepared and used as catalysts in hydrogenation of benzene. Their catalytic activities were obviously relative with the compositions or structures of these complexes. The hydrogenations of benzene catalyzed by complexes **1**, **2** and **3** were homogeneous in the conditions of reaction temperature of 100 °C and hydrogen pressure of 50 kg/cm^2, complexes **4**, **5** and **6** were simultaneously homogeneous and heterogeneous in the same reaction conditions. Among all complexes, **4**, **5** and **6** were of higher catalytic activities than **1**, **2** and **3**. The dinuclear complex **6** in which one chlorine anion was substituted by one tetrafluoroborate gave the highest activity. The higher activities of complex **4**, **5** and **6** were owing to the easy generation of catalytic active species and the formations of Ru(0) particles which were of the highly catalytic activity. As novel complexes, the compositions and structures of **1**, **2**, **4** and **5** were characterized by NMR spectra. The structures of **4** and **5** were further determined by elemental analysis and single crystal X-ray diffraction.
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1. Introduction

The catalytic hydrogenation of arene is a fascinating area of research in which many highly innovative and imaginative catalyst systems have been developed. Some of catalysts were applied on ranging from small-scale synthesis [1] to industrial processes [2,3], especially, in the field of heterogeneous catalysis. However, the studies on using complexes as catalysts for the hydrogenation of benzene were rare. Halpern and co-workers [4] used a cationic rhodium complex containing a phosphine ligand, [Rh(dppe)(MeOH)$_2$]$^+$ (dppe = 1,2-bis(diphenylphosphino)ethane), as catalyst for

the hydrogenation of arene and found that this complex was effective to catalyze the reaction. Fink and co-workers [5a–d] reported the catalytic properties of a number of cluster compounds, such as (η^6-C$_6$H$_6$)$_2$Ru$_2$Cl$_4$, [(η^6-C$_6$H$_6$)$_4$Ru$_4$H$_4$]Cl$_2$, [(η^6-C$_6$H$_6$)$_4$Ru$_4$H$_6$]Cl$_2$, [(η^6-C$_6$Me$_6$)$_2$(η^6-C$_6$H$_6$)Ru$_3$(μ$_2$-H)$_3$(μ$_3$-O)]$^+$ and [(η^6-C$_6$Me$_6$)$_2$(η^6-C$_6$H$_6$)Ru$_3$(μ$_2$-H)$_2$(μ$_2$-OH)(μ$_3$-O)]$^+$ in the hydrogenation of arene and found that these cluster compounds were of the high catalytic activities in aqueous–organic biphasic system. TOF of 5466 h^{-1} for the hydrogenation of benzene was obtained by using [(η^6-C$_6$Me$_6$)$_2$(η^6-C$_6$H$_6$)Ru$_3$(μ$_2$-H)$_2$(μ$_2$-OH)(μ$_3$-O)]$^+$ as catalyst and the cluster could be recovered as tetrafluoroborate salt after the catalytic run [5e]. Dyson and co-workers [6,7] studied on a series of ruthenium complexes containing phosphine ligands [(η^6-*p*-cymene)(dppm)RuCl]Cl, [(η^6-*p*-cymene)RuCl$_2$]$_2$(μ$_2$-dppe), (η^6-*p*-cymene)(dppe)RuCl$_2$, and (η^6-*p*-cymene)(η^1-dppm)RuCl$_2$ (dppm = 1,2-bis(diphenylphosphino)methane) for

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benzene hydrogenation, and observed the effect of pH on the hydrogenation of benzene in an aqueous–organic biphasic system in the presence of [(η^6-p-cymene)(η^2-dppm)RuCl]Cl, and thought Ru(0) was the real active species for the hydrogenation.

Recently, the interest of researchers was mainly focused on determining the really active species formed in the hydrogenation of benzene when a complex was used as catalyst [8a,b]. The research results indicated that many complexes, which were thought to be the homogeneous catalysts in past, were decomposed and reduced into metal particles in the conditions of benzene hydrogenation reaction, thus they were really the heterogeneous catalysts. Finke and co-workers [9] found that the really active species of Ru(II)–(η^6-C_6Me_6)(OAc)$_2$ was the metal nanocluster formed from the complex decomposition. [(η^6-C_6Me_6)$_2$(η^6-C_6H_6)Ru$_3$(μ_2-H)$_3$(μ_3-O)]$^+$, which was thought to be highly active homogenous catalyst [5c], was demonstrated to be a heterogoneous catalyst [8b]. Even though the low activity (TOF 1.6 h^{-1}) complex [RuH$_2$(H$_2$)$_2$(PCy$_3$)$_2$] was considered to be homogeneous [10a], it was still proved to be a heterogeneous [10b]. Real homogeneous catalysts were rare in hydrogenation of benzene. Among them, Nb(CH$_2$SiMe$_3$)(P$_2$N$_2$) (P$_2$N$_2$ = RP(CH$_2$SiMe$_2$NSiMe$_2$NSiMe$_2$CH$_2$)$_2$PR and R = Cy or Ph) [11a], Ta (η^5-C_4NMe_4)(NC$_4$H$_4$)Me$_3$ [11b] and W(CO)$_3$-(MeCN)(tppms)$_2$ (tppms = 3-sulfonatophenyldiphenylphosphine sodium salt) [12] were examples. However, it is not clear up to date that how the composition and structure of a complex affect its catalytic activity and stability in the hydrogenation of benzene, why some complexes are real homogeneous catalyst, and other complexes become heterogeneous one.

Herein, six Ru–η^6-C_6H_6-diphosphine complexes that were of the different kinds of structures and contained the different phosphine ligands were synthesized (Scheme 1) and used as catalysts in benzene hydrogenation. The relationship between the compositions or structures of complexes and the turnover frequency of the hydrogenation was investigated. It was found the stabilities of these complexes were greatly changes with their compositions or structures in the same reaction conditions.

2. Experimental

2.1. Materials

All synthetic reactions were performed with standard Schlenk technique and under nitrogen atmosphere. Solvents were dried over appropriate drying agent and distilled under nitrogen prior to use. BISBI (2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl) [13], BDPX (1,2-bis(diphenylphosphinomethyl)benzene) [14], BDNA (1,8-bis(diphenylphosphinomethyl)naphthalene) [15], [RuCl(η^6-C_6H_6)]$_x$ [16], complex **3** and **6** [17] were prepared according to reported methods.

2.2. Analytical methods

The complexes **1**, **2**, **4** and **5** were dissolved in CDCl$_3$, and their ^{1}H and ^{31}P $\{^1$H$\}$ NMR spectra were recorded on Bruker DPX 400 spectrometer at room temperature, 400.13 MRz for ^{1}H and 160.97 MHz for ^{31}P. The chemical shifts of ^{31}P $\{^1$H$\}$ NMR were relative to 85% H$_3$PO$_4$ as external standard, ^{1}H NMR relative to TMS as internal standard, with downfield shifts as positive.

The single crystals were grown in the mixture solvent of CH$_2$Cl$_2$, CH$_3$OH and Et$_2$O. Their structures were determined on a Rigaku RAXIS IIC imaging-plate diffractometer. Intensity data were collected using graphite-monochromatized Mo Kα (λ = 0.71073 Å) radiation from a rotating-anode generator operating at 50 kV and 90 mA. All calculations were performed with Siemens SHELXTL PLUS (PC Version) system.

2.3. Catalytic reaction

Benzene hydrogenation was preformed in a stainless steel autoclave (30 ml) with a glass liner and a magnetic stirring bar. The desired amount of ruthenium complex and benzene were introduced into the autoclave, and it was closed and replaced with pure H$_2$ for five times, and then was pressurized to 50 atm with H$_2$. When the autoclave was heated to the desired tempera-
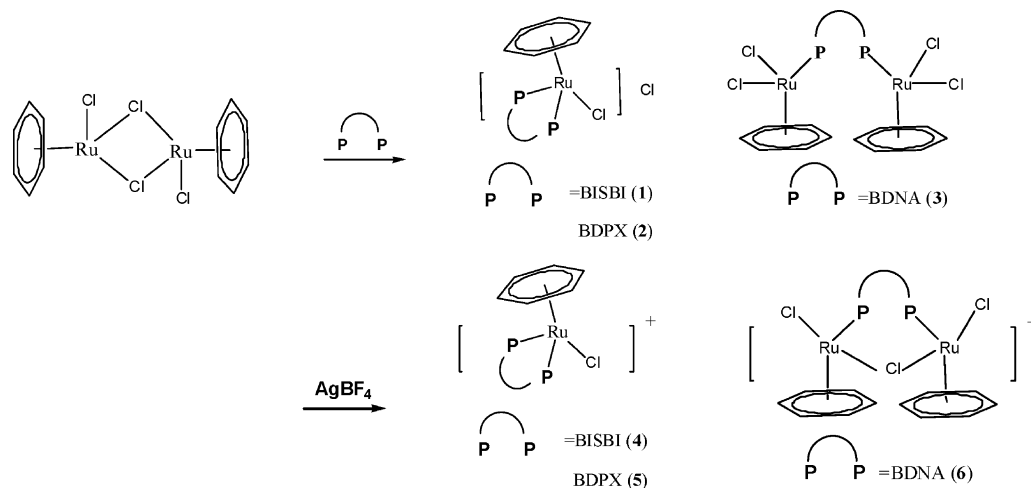
Scheme 1. Structures of complexes.

ture, the stirrer was turn on, and the reaction time was accounted. The conversion of benzene hydrogenation was analyzed by GC-9790 with FID detector (detecting temperature of 250 °C) and PEG-20 M supelco column (30 m × 0.25 mm, 0.25 μm film) at 55 °C

3. Preparations of ruthenium complex 1, 2, 4, and 5

3.1. [RuCl (η⁶-C₆H₆)(BISBI)]Cl (**1**)

A mixture of $[RuCl_2(\eta^6\text{-}C_6H_6)]_x$ (0.100 g, 0.40 mmol) and BISBI (0.220 g, 0.40 mmol) in 50 ml methanol was stirred at room temperature for 20 h. The solid substances were slowly dissolved and the color of solution changed to yellowish brown with small amount of white precipitate. At the end of reaction, the solution was filtered to remove the white precipitate and followed by solvent removal under vacuum to give 0.295 g brown solid. Yield: 92%. $^{31}P \{^1H\}$ NMR: δ(ppm), 14.29 (d), 23.47 (d).

3.2. [RuCl(η⁶-C₆H₆)(BDPX)]Cl (**2**)

Complex **2** was prepared by the similar procedure as complex **1**. Yield: 87%. $^{31}P \{^1H\}$ NMR: δ(ppm) 20.73 (s).

3.3. RuCl (η⁶-C₆H₆) (BISBI)] BF₄ (**4**)

A suspension of $[RuCl(\eta^6\text{-}C_6H_6)(BISBI)]Cl$ (0.160 g, 0.20 mmol) and AgBF₄ (0.040 g, 0.20 mmol) in the mixture solvent of CH_2Cl_2 (7 ml) and methanol (10 ml) was stirred for 2 h at room temperature, and then formed AgCl was filtered off. The filtrate was evaporated to about 6 ml under vacuum and was put in refrigerator over night to give a lot of brown red crystals. The crystals were filtered, washed for two times with methanol, and then dried in vacuum. 0.106 g brown crystals were obtained. Yield: 62.3%. Calc. for $C_{46}H_{42}BCl_5F_4P_2Ru$: C, 54.04; H, 4.11; found: C, 54.36; H, 4.12. $^{31}P \{^1H\}$ NMR: δ(ppm) 15.55 (d), 25.00 (d), Jpp = 54.2 Hz. ^1H NMR: δ(ppm) 3.48 (s, 4H), 5.31 (s, 6H), 6.80–7.70 (m, 28H).

3.4. [RuCl (η⁶-C₆H₆) (BDPX)] BF₄ (**5**)

Complex **5** was prepared by using complex **2** as starting materials, and the same procedure as complex **4**. Yield: 82%. Calc. for $C_{39}H_{36}BCl_3F_4P_2Ru$: C, 54.39; H, 4.18; found: C, 54.49; H, 4.10. $^{31}P \{^1H\}$ NMR: δ(ppm) 22.44 (s). ^1H NMR: δ(ppm) 3.45 (s, 4H), 5.67 (s, 6H), 7.00–8.00 (m, 24H)

4. Results and discussion

In order to compare the activities of mononuclear complexes bearing diphosphine ligands with dinuclear complexes, mononuclear complexes **1**, **2**, **4** and **5** in which one ruthenium atom was coordinated by a BISBI or a BDPX and the dinuclear complexes **3** and **6** in which two ruthenium atoms shared a BDNA were prepared. The reaction equations and structures of all Ru–η⁶-C₆H₆-diphosphine complexes were illustrated in Scheme 1.

4.1. Structures of complexes

Solid complexes **1**, **2**, **4** and **5** were stable in air, but their solutions were sensitive to air. After the solution was exposed to air for a few minutes, its color would change from yellowish brown to green. Two doublets in $^{31}P \{^1H\}$ NMR of complex **1** and **4** indicated that the coordination environments of the two phosphorus atoms in BISBI were different because of the diastereoisomer of the backbone of biphenyl in coordinated BISBI. After one tetrafluoroborate group exchanged one chlorine anion in complex **1**, the chemical shift changed from 14.25 and 23.47 to 15.55 and 25.00 ppm, respectively. The chemical shift 5.31 ppm of the protons on the coordinated phenyl ring in ^1H NMR spectrum was in agreement with result reported in literature [18].

A singlet at 20.73 ppm in $^{31}P \{^1H\}$ NMR of complex **2** suggested that the chemical environments of two phosphorus atoms were equivalent. The complex **5** was formed by one tetrafluoroborate substituting one chlorine anion in complex **2** and its ^{31}P NMR spectrum shifted to 22.44 from 20.73 ppm without substitution. ^1H NMR spectrum of complex **5** showed that protons of methylene of BDPX appeared as a singlet at 3.50 ppm and the protons on coordinated phenyl ring also appeared as a singlet at 5.67 ppm. According to the results of NMR spectra and elemental analysis of complex **4** and **5**, they were mononuclear complexes in which each ruthenium atom was coordinated by a phenyl ring, a chlorine anion and a diphosphine. Because complex **1** and **2** were the similar with complexes **4** and **5** respectively, complex **1** and **2** did not characterized by elemental analysis. The proposal structures were shown in Scheme 1. The single crystal X-ray diffraction of complex **4** and **5** further confirmed the results from NMR and elemental analysis. Their crystal data were listed in Table 1 and their structures of the single crystal X-ray diffraction were shown in Figs. 1 and 2, respectively. The selected bond lengths and bond angles of complexes **4** and **5** were listed in Table 2. The bond length of Ru–P (1) 2.3670 Å was slightly different from that of Ru(1)–P(2) 2.3772 Å in complex **4**, and both were little longer than that of Ru(1)–P(1) 2.3295 Å, Ru(1)–P(2) 2.3764 Å in complex **5**, Ru(1)–P(1) 2.329 Å, Ru(1)–P(2) 2.336 Å in complex $[(\eta^6\text{-}p\text{-cymene})(dppe)RuCl]BF_4$ [7] and Ru(1)–P(1) 2.316 Å, Ru(1)–P(2) 2.309 Å in complex $[(\eta^6\text{-}p\text{-cymene})(dppm) RuCl]BF_4$ [7]. They were very close to the bond length in some binuclear complexes, such as Ru(1)–P(1) 2.345 Å, Ru(1)–P(2) 2.357 Å in complex **3**, and Ru(1)–P(1) 2.3471 Å, Ru(1)–P(2) 2.3767 Å in complex $[Ru_2Cl_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-BDNA})_2](BF_4)_2$ [17]. The bond length of Ru–C (average 2.248 Å) in complex **5** was slightly shorter than 2.258 Å in complex **4**, all Ru–C in complexes **4** and **5** were longer than Ru(1)–C (average 2.188 Å) and Ru(2)–C (average 2.175 Å) in complex **6**. The bond angle of P(1)–Ru(1)–P(2) in complex **4** was 98.62°. It was larger than 95.94° in complex **5**, obviously larger than 91.4° in $[(\eta^6\text{-}C_6H_6)RuCl(BINAP)]^+$ [18] and much larger than 83.03° in $[(\eta^6\text{-}p\text{-cymene})(dppe)RuCl]BF_4$ or 71.29° in $[(\eta^6\text{-}p\text{-cymene})(dppm)RuCl]BF_4$ because the size of chelating ring and the backbone of ligand increased in the order of dppm < dppe < BDPX < BISBI.

Table 1
Crystal data for complex **4** and **5**

	Complexes	
	4	**5**
Empirical formula	$C_{45}H_{40}BCl_3F_4P_2Ru$	$C_{38}H_{35}BClF_4O_{0.50}P_2Ru$
Formula weight	936.94	784.93
Temperature (K)	294(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P1$	$P2_1/c$
Unit cell dimensions	$a = 11.916(2)$ Å $\alpha = 69.43(3)°$ $b = 14.544(3)$ Å	$a = 11.8570(2)$ Å $\alpha = 90°$ $b = 13.9800(7)$ Å
	$\beta = 81.00(3)°$ $c = 14.744(3)$ Å $\gamma = 72.27(3)°$	$\beta = 93.316(4)°$ $c = 20.9300(11)$ Å $\gamma = 90°$
Volume, z	2275.2(8) Å^3, 2	3463.6(3) Å^3, 4
Density (calculated) (mg/m^3)	1.368	1.505
Absorption coefficient (mm^{-1})	0.637	0.673
$F(0\,0\,0)$	952	1596
Crystal size (mm)	0.38 mm × 0.32 mm × 0.28 mm	0.40 mm × 0.40 mm × 0.30 mm
θ Range for data collection	1.48°–25.62°	1.75°–25.73°
Limiting indices	$-14 \leq h \leq 13, -17 \leq k \leq 0, -17 \leq l \leq 16$	$0 \leq h \leq 14, -16 \leq k \leq 16, -25 \leq l \leq 25$
Reflections collected	7338	11200
Independent reflections	7338 ($R_{int} = 0.0000$)	5975 ($R_{int} = 0.0437$)
Absorption correction	Semi-empirical	ABSCOR
Maximum and minimum transmission	1.175 and 0.794	
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7281/14/693	5960/0/429
Goodness-of-fit on	0.821	1.063
Final R indices [$I > 2_-(I)$]	$R1 = 0.0582, wR2 = 0.1762$	$R1 = 0.0507, wR2 = 0.1413$
R indices (all data)	$R1 = 0.0676, wR2 = 0.2268$	$R1 = 0.0550, wR2 = 0.1538$
Extinction coefficient	0.0096(6)	0.0121(11)
Largest diff. peak and hole	0.828 and -0.771e Å^{-3}	0.840 and -0.749e Å^{-3}

4.2. Benzene hydrogenation

The results in Table 3 showed that the catalytic activities of complexes for the hydrogenation of benzene obviously changed with their structures and compositions. When complex **1**, **2** and **3** were used as catalysts, their reaction solutions were homogeneous and no black particles of metal ruthenium were observed at the end of reaction. The solution colors of complexes **1** and
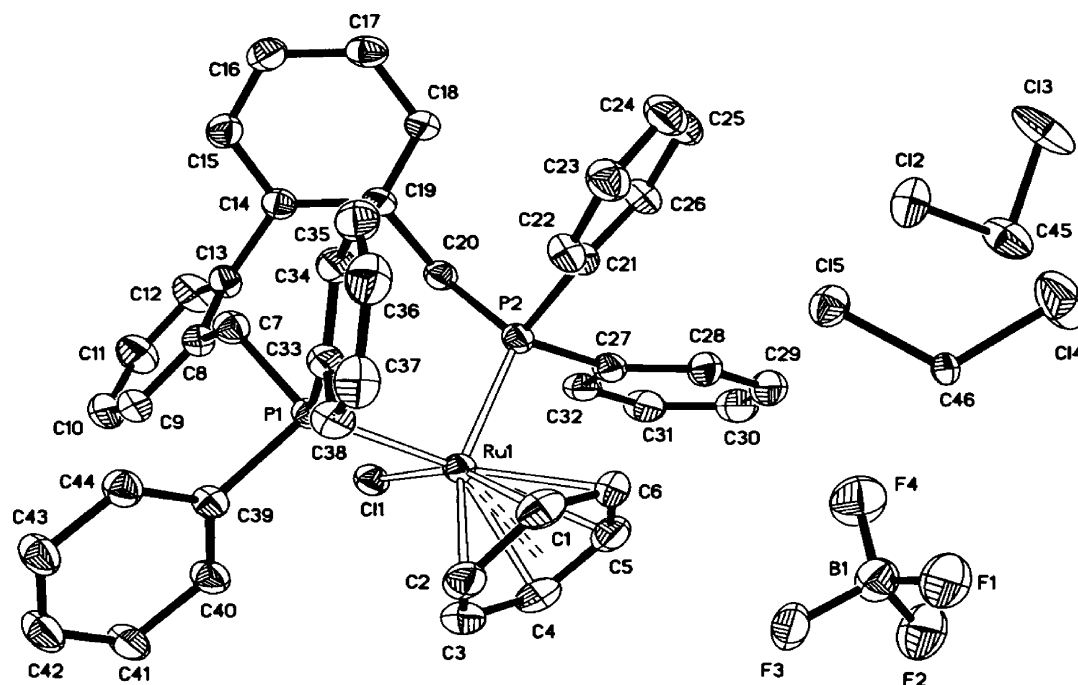

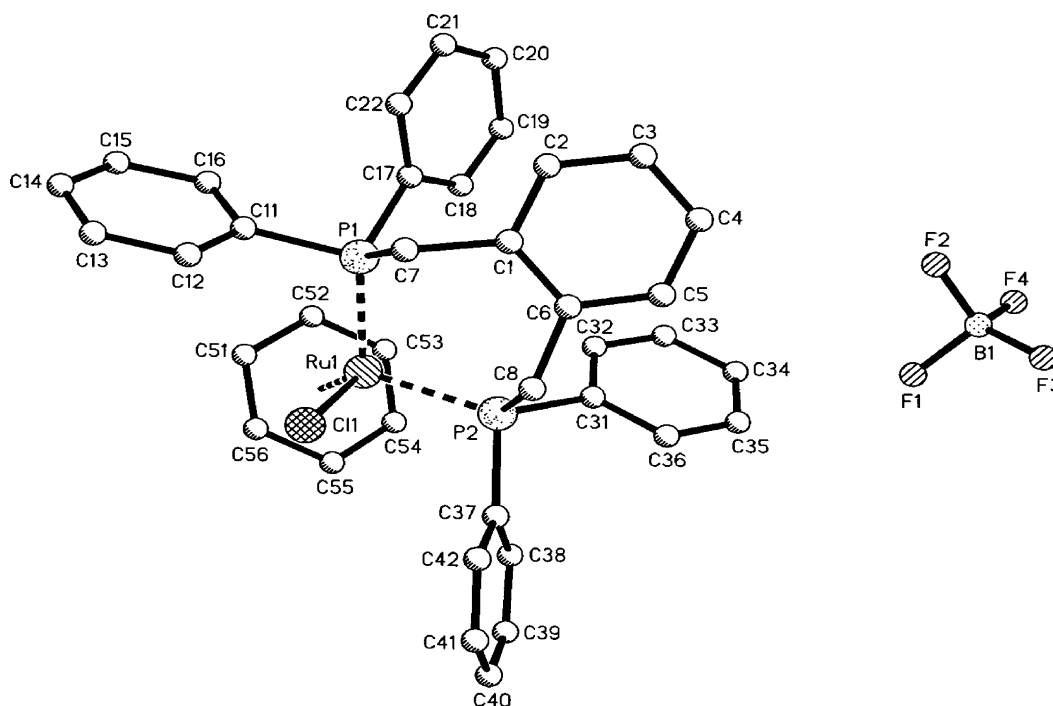Fig. 1. Single crystal structure of complex **4**.

Fig. 2. Single crystal structure of complex **5**.

2 were yellowish brown, and complex **3** was reddish brown. These colors of the solutions gradually changed to dark green, even black in air. This color change in air is a typical character for the analogous ruthenium complexes bearing phosphine ligands. These showed that the ruthenium–phosphine complexes did not be decomposed and reduced to metal particles in the reaction conditions. If no complex was added into the autoclave, the hydrogenation product was not detected at the end of reaction. This proved that the hydrogenation was catalyzed by the added

complex, and not by the metal particles that could be adsorbed on the surface of glass liner.

Of course, if the small amount of nanoclusters were formed and played the catalytic role, these nanoclusters could not be seen by visual observation. In order to clarify that the really active species was homogeneous or heterogeneous in the reaction, the mercury poisoning experiment, which was considered as a most effective method to distinguish homogeneous and heterogeneous catalysis [19,8a,8b], was carried out. In the experiment, the rigorous stirring and the addition of excess mercury were needed to make mercury be fully dispersed and a reliable result be obtained. Our experiment had demonstrated that the mass transfer limitation in the dissolution of hydrogen gas could be eliminated when the stirring rate was over 200 rpm, so the stirring rate of 1500 rpm and the molar ration of 140:1 of mercury to complex were chosen. When both mercury and complex **1** were added to autoclave in the beginning of reaction, the activity of complex **1** was consistent with that without mercury. Complex **2** and **3** gave the similar results, too (Tables 3 and 4). This confirmed that when these complexes were used as catalysts, the hydrogenation of benzene could be homogeneous.

Table 2
Selected bond lengths (Å) and angles (°) of complex **4** and **5**

Complex **4**		Complex **5**	
Bond	Lengths or angles	Bond	Lengths angles
Ru(1)–C(1)	2.230(2)	Ru(1)–C(51)	2.285(3)
Ru(1)–C(2)	2.258(2)	Ru(1)–C(52)	2.237(3)
Ru(1)–C(3)	2.278(2)	Ru(1)–C(53)	2.250(4)
Ru(1)–C(4)	2.292(2)	Ru(1)–C(54)	2.231(4)
Ru(1)–C(5)	2.285(2)	Ru(1)–C(55)	2.239(4)
Ru(1)–C(6)	2.206(2)	Ru(1)–C(56)	2.244(3)
Ru(1)–P(1)	2.3670(8)	Ru(1)–P(1)	2.3295(9)
Ru(1)–P(2)	2.3772(9)	Ru(1)–P(2)	2.3764(9)
Ru(1)–Cl(1)	2.3981(6)	Ru(1)–Cl(1)	2.3970(9)
P(1)–Ru(1)–P(2)	98.62(3)	P(1)–Ru(1)–P(2)	95.94(3)
P(1)–Ru(1)–Cl(1)	88.48(3)	P(1)–Ru(1)–Cl(1)	84.19(3)
P(2)–Ru(1)–Cl(1)	84.81(4)	P(2)–Ru(1)–Cl(1)	82.07(3)
C(39)–P(1)–Ru(1)	112.93(5)	C(17)–P(1)–Ru(1)	120.48(12)
C(7)–P(1)–Ru(1)	123.74(6)	C(11)–P(1)–Ru(1)	108.24(11)
C(33)–P(1)–Ru(1)	113.51(5)	C(7)–P(1)–Ru(1)	117.55(12)
C(21)–P(2)–Ru(1)	117.63(5)	C(31)–P(2)–Ru(1)	121.20(12)
C(27)–P(2)–Ru(1)	107.68(4)	C(37)–P(2)–Ru(1)	108.94(12)
C(20)–P(2)–Ru(1)	122.02(5)	C(8)–P(2)–Ru(1)	118.59(12)

Table 3
Effect of compositions or structures of complexes on hydrogenation

Complex	**1**	**2**	**3**	**4**	**5**	**6**	**0**[a]
Conversion (%)	3.3	1.9	6.7	27.7	19.7	37.2	0.0
TOF (h^{-1})	7.4	4.3	15.1	62.5	44.5	83.9	0.0

Conditions: benzene, 1 ml; complex, 0.0050 mmol; H$_2$, 50 atm; temperature, 100 °C; reaction time, 10 h; stirring rate, 1500 rpm.

[a] No catalyst.

Table 4
Effect of mercury addition on hydrogenation

Complex	1	2	3	4	5
Conversion (%)	3.2	1.7	6.7	23.5	15.7
TOF (h^{-1})	7.2	3.8	15.1	53.0	35.4

Conditions: benzene, 1 ml; complex, 0.0050 mmol; H_2, 50 atm; temperature, 100 °C; reaction time, 10 h; mercury, 0.69 mmol; stirring rate, 1500 rpm.

Furthermore, the relationship between conversion and time was investigated by using complex **2** as catalyst. The result was shown in Fig. 3 and it was almost a straight line. The induction period of catalytic reaction, the burst increase period of catalytic activity and the deactivation of catalyst were not observed in our experimental conditions. In the same time, these data showed a good repeatable. All of these were the basic characters of homogeneous catalysis.

However, some ruthenium black precipitates appeared in the bottom of the glass liner at the end of reaction when complex **4**, **5** and **6** (in which a chlorine anion was exchanged by $BF_4{}^-$) were used as catalysts. The phenomenon indicated that part of these complexes could be decomposed and reduced into metal ruthenium particles. The colors of the solutions changed from brown to green or deep green while they contacted with air. The catalytic activities of complexes **4**, **5** and **6** were much higher than their analogue complexes **1**, **2** and **3**. The results indicated that the substitution of one chlorine anion with one $BF_4{}^-$ was not favorable to stabilize the complex. The mercury poisoning experiment for complex **5** indicated that the addition of mercury in the beginning of reaction would decrease the conversion of benzene hydrogenation from 19.7 to 15.7% (Tables 3 and 4). This result exhibited about 4% among the conversion 19.7% was contributed by the hydrogenation of metal ruthenium particles and most of the conversion of 19.7% resulted from homogeneous catalyst. Compared with the result of complex **2** in the same reaction conditions, the complex **5** that was generated by substituting one chlorine anion of complex **2** with one tetrafluoroborate
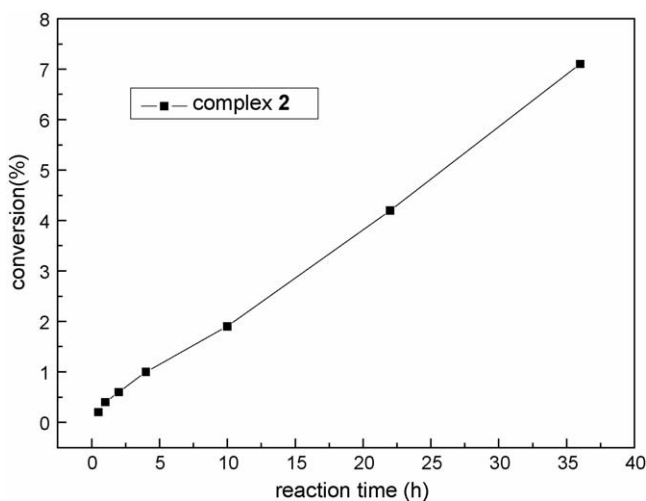
showed much higher catalytic activity. Similarly, the higher catalytic activities of complex **4** and **6** than complex **1** and **3** could be owing to the easy formation of the catalytic active species. In some homogeneous catalysis, excess ligand was generally introduced into reaction system to protect the complex catalyst from decomposition during reaction. If extra BDPX was introduced to the reaction solution of complex **5** and the molar ratio of BDPX to complex **5** was 1:1, the black precipitates disappeared at the end of reaction and the conversion of benzene hydrogenation decreased to 10.4%. When both mercury and extra BDPX were added to the reaction system catalyzed by complex **5** at the beginning, the conversation was 9.6%. Therefore, the addition of extra ligand could improve the stability of the complex in the catalytic process. Among these complexes, binuclear complex **3** showed a higher activity than the mononuclear complexes **1** and **2**, and binuclear complex **6** showed higher activity than the mononuclear complexes **4** and **5**. This suggested that the catalytic active centers in binuclear complexes would form more easily than that in mononuclear compounds under the reaction conditions, or two ruthenium atoms played a cooperation role in the activation of H_2 and benzene. The study on the activation mechanism of the binuclear complexes for H_2 and benzene are progressing in our research group.

5. Conclusion

The studies demonstrated that complexes **1**, **2** and **3** were homogeneous catalysts in hydrogenation of benzene. However, complexes **4**, **5** and **6** were partly decomposed in the same hydrogenation conditions, thus the catalytic reactions of them were simultaneously homogeneous and heterogeneous. The addition of extra phosphine ligand was favorable to stabilize the complex in the catalytic process.

Fig. 3. Curve of conversion with time. *Reaction conditions:* complex 2, 0.005 mmol; benzene, 1 ml; pressure, 50 atm; temperature, 100 °C and stirring rate, 1500 rpm.

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