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Syntheses and crystal structures of binuclear ruthenium complexes bearing 1,8′-bis(diphenylphosphinomethyl)naphthalene

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Abstract

Treatment of $[RuCl_2(\eta^6\text{-}C_6H_6)]_x$ with bidentate phosphine ligand BDNA [1,8-bis(diphenylphosphinomethyl)naphthalene] in methanol at room temperature gave η^6-benzene-ruthenium complexes $Ru_2Cl_4(\eta^6\text{-}C_6H_6)_2(\mu\text{-BDNA})$ (**1**). Complex **1** further reacted with $AgBF_4$ to form complex $[Ru_2Cl_2(\mu\text{-Cl})(\eta^6\text{-}C_6H_6)_2(\mu\text{-BDNA})](BF_4)$ (**2**). $[RuCl_2(\eta^6\text{-}C_6H_6)]_x$ reacted with BDNA in refluxing methanol and then the reaction solution was treated with $AgBF_4$ to generate complex $[Ru_2Cl_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-BDNA})_2](BF_4)_2$ (**3**). Their compositions and structures had been determined by elemental analyses, NMR spectra and single crystal X-ray diffractions. X-ray diffraction showed that complex **1** belonged to monoclinic crystal system, $P2_1/c$ space group with $Z = 4$, $a = 12.810$ Å, $b = 21.507$ Å, $c = 18.471$ Å, $\beta = 107.95°$; complex **2** belonged monoclinic crystal system, $P2_1/n$ space group with $Z = 4$, $a = 14.498$ Å, $b = 15.644$ Å, $c = 20.788$ Å, $\beta = 103.404°$, and complex **3** belonged to monoclinic crystal system, $P2_1/n$ space group with $Z = 2$, $a = 13.732$ Å, $b = 14.351$ Å, $c = 19.733$ Å, $\beta = 94.82°$.

Keywords: Ruthenium; 1,8′-Bis(diphenylphosphinomethyl)naphthalene; Binuclear complex

1. Introduction

The reaction of cyclohexa-1,3-diene with ethanolic ruthenium(III) trichloride to give insoluble benzene complex of empirical formula $[RuCl_2(C_6H_6)]_x$ was originally reported by Winkhaus and Singer [1]. This polymer is very easy to react with other ligands to form mononuclear or binuclear complexes. Because these complexes are generally excellent hydrogenation catalysts for unsaturated organic compounds [2–9], the reactions of $[RuCl_2(\eta^6\text{-}C_6H_6)]_x$ with a variety of monodentate nucleophiles and bidentate phosphine have been an active research area [10–29]. Treatment of $[RuCl_2(\eta^6\text{-}C_6H_6)]_x$ with monodentate nucleophiles (tertiary phosphine, pyridine, tertiary arsine, etc.) would generally give $(\eta^6\text{-}C_6H_6)RuCl_2L$ and $[(\eta^6\text{-}C_6H_6)RuClL_2]Cl$ as products (Scheme 1) [13–15]. However, the reaction of $[RuCl_2(\eta^6\text{-}C_6H_6)]_x$ with bidentate phosphines are much more complicated [13,15,18–20]. In general, when the backbone of bidentate phosphine is flexible, such as $Ph_2P(CH_2)_nPPh_2$, the main product would be mononuclear species $[(\eta^6\text{-}C_6H_6)Ru(P\text{-}P)Cl]^+$ **B** or phosphine-bridged binuclear complex $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}P\text{-}P)\text{-}Ru(\eta^6\text{-}C_6H_6)]$ **D** at lower reaction temperature (Scheme 2). When the bidentate phosphine is of bulky or rigid backbone, such as BINAP [2,2′-bi(diphenylphosphino)-1,1′-binaphthalene], BPPB [1,2-bis(diphenylphosphino)benzene], high yields of $[(\eta^6\text{-}C_6H_6)Ru(P\text{-}P)Cl]^+$ **B** would be obtained. When the backbone of bidentate phosphine is smaller, such as DPPE [1,2-bis(diphenylphosphino)ethane], **C** would be the principal product. Most of bidentate phosphine ligands could not form product **B** or **D** in high yields. Their products are often the mixtures of **B**, **C**, and **D**, and

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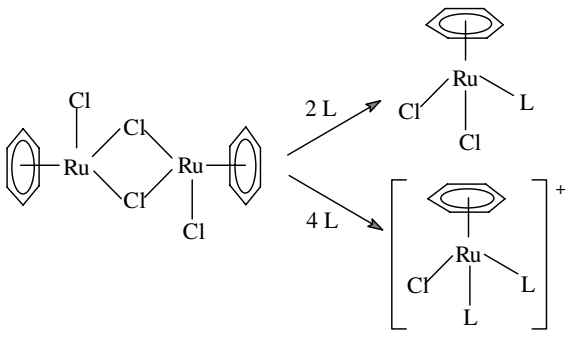


Scheme 1. Reactions of $[RuCl_2(\eta^6\text{-}C_6H_6)]_x$ with monodentate nucleophiles.

the isolation of the mixtures is very difficult. Sometimes, $[RuCl_2(C_6H_6)]_x$ has to be converted into $[\eta^6\text{-}(C_6H_6)Ru(CH_3CN)_2Cl]^+$ or $[\eta^6\text{-}(C_6H_6)RuCl_2(DMSO)]$ [23], and then they were used as starting materials for synthesis of above-mentioned Ru-diphophosphine complexes. Therefore, only a few examples are known for the formation of $[(\eta^6\text{-}C_6H_6)\text{-}Ru(\mu\text{-}P\text{-}P)Ru(\eta^6\text{-}C_6H_6)]$.

In recent, Girolami and P. Stoppioni et al. reported the synthesis of a new kind of complexes $Cp_2Ru_2(\mu\text{-}Ph_2PCH_2PPh_2)(AlH_5)$, $[\{CpRu(CH_3CN)_2\}_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)](PF_6)_2$ and $[\{CpRu(CH_3CN)_2\}_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)_2](PF_6)_2$ by the reaction of $(CpRhCl)_4$ and $[CpRu(CH_3CN)_3]PF_6$ with the smaller backbone bidentate phosphine $Ph_2PCH_2PPh_2$ and $Ph_2PCH_2CH_2PPh_2$ [16]. Yamamoto [22] synthesized $[\{(\eta^6\text{-arene})RuCl_2\}_2(\mu\text{-BDNA})]$ (arene = substituted benzene) by reacting BDNA with $[(\eta^6\text{-arene})RuCl_2]_x$ in CH_2Cl_2. $[\{(\eta^6\text{-arene})RuCl_2\}_2\text{-}(\mu\text{-BDNA})]$ reacted further with AgOTf to obtain $[\{(\eta^6\text{-arene})Ru(\mu\text{-Cl})\}_2(\mu\text{-BDNA})](OTf)_2$.

Herein, we would like to report the synthesis of three novel complexes $Ru_2Cl_4(\eta^6\text{-}C_6H_6)_2(\mu\text{-BDNA})$ **1**, $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-BDNA})(\mu\text{-Cl})RuCl(\eta^6\text{-}C_6H_6)](BF_4)$ **2** and $[Ru_2Cl_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-BDNA})_2](BF_4)_2$ **3** with satisfying yield by the reaction of $[RuCl_2(C_6H_6)]_x$ with a larger backbone bidentate phosphine BDNA in methanol. Especially the structure types of complexes **2** and **3** were firstly reported.

2. Experimental

2.1. Materials

All synthetic reactions were performed with standard Schlenk technique and under nitrogen atmosphere. Solvents were dried over appropriate drying agents and distilled under nitrogen prior to use. $[RuCl_2(C_6H_6)]_x$ [1], BDNA [30] were prepared according to the reported methods.

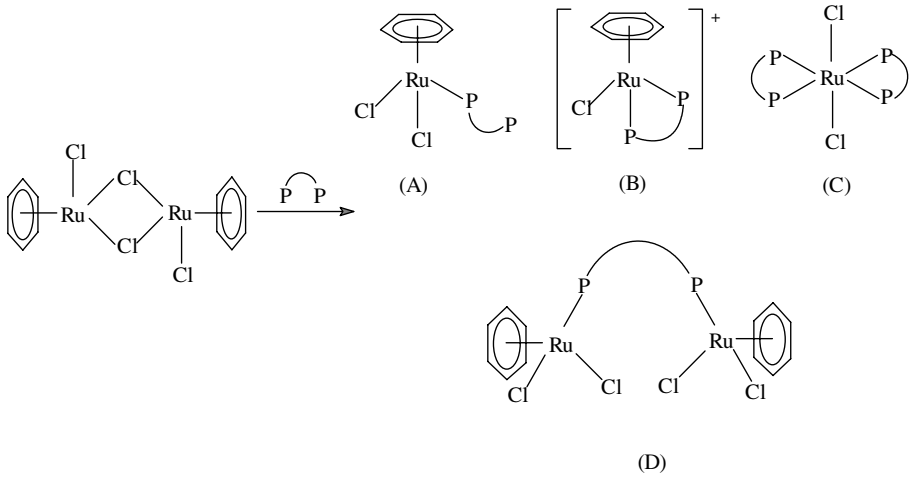
2.2. Analytical methods

All samples were dissolved in $CDCl_3$, and their ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker DPX 400 spectrometer at room temperature, 400.13 MHz for ^1H and 160.97 MHz for ^{31}P. The chemical shifts of $^{31}P\{^1H\}$ NMR were relative to 85% H_3PO_4 as external standard, ^1H NMR relative to TMS as internal standard, with downfield shifts as positive. Elemental analyses were performed by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

3. Preparation of complexes

3.1. $[(\eta^6\text{-}C_6H_6)RuCl_2(\mu\text{-BDNA})Ru(\eta^6\text{-}C_6H_6)Cl_2]$ 1

A mixture of $[RuCl_2(C_6H_6)]_x$ (0.125 g, 0.5 mmol) and BDNA (0.270 g, 0.5 mmol) in 50 ml methanol was stirred at room temperature for 24 h. During the time, brown solid $[RuCl_2(C_6H_6)]_x$ was slowly dissolved, the solution changed to orange brown with the formation of orange-red precipitates. At the end of reaction, the solvent was completely evaporated under vacuum and an orange solid was



Scheme 2. Reaction of $[RuCl_2(\eta^6\text{-}C_6H_6)]_x$ with bidentate phosphines.

obtained. The solid was recrystallised in the mixture of 1:2 of CH_2Cl_2 to CH_3OH to form a lot of beautiful red crystals. The product was filtered and washed with a mixture (1:2) of methanol to diethyl ether to give 0.15 g red crystals. Yield: 58%. Calc. for $C_{48}H_{48}Cl_4O_3P_2Ru_2$: C, 53.44; H, 4.48. Found: C, 52.93; H, 4.51. $^{31}P\{^1H\}$ NMR: δ (ppm) 33.18 (s). ^1H NMR: δ (ppm) 3.49 (s, 4H), 5.35 (s, 12H), 6.6–7.5 (m, 26H).

3.2. $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}BDNA)(\mu\text{-}Cl)RuCl(\eta^6\text{-}C_6H_6)](BF_4)$ 2

A suspension of $[(\eta^6\text{-}C_6H_6)RuCl_2(\mu\text{-BDNA})Ru(\eta^6\text{-}C_6H_6)Cl_2]$ (0.102 g, 0.1 mmol) and $AgBF_4$ (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 precipitated AgCl was filtered off. The filtrate was evaporated to about 6 ml in vacuum and was put in refrigerator over night. A lot of brown red crystals were formed. The crystals was filtered, washed for two times with methanol, and then dried in vacuum. 0.0675 g red crystals were obtained (yield 63%). Calc. for $C_{49}H_{46}BCl_3F_4OP_2Ru_2$: C, 53.11; H, 4.18. Found: C, 52.95; H, 4.21. ^1H NMR ($CDCl_3$) δ (ppm): 3.48 (s, 4H), 5.85 (s, 12H), 6.59–7.66 (m, 26H). $^{31}P\{^1H\}$ NMR: δ (ppm) 29.48.

3.3. $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}BDNA)_2RuCl(\eta^6\text{-}C_6H_6)](BF_4)_2$ 3

0.063 g (0.25 mmol) of $[RuCl_2(\eta^6\text{-}C_6H_6)]_x$ and 0.27 g (0.5 mmol) of BDNA were suspended in 30 ml methanol. The mixture was refluxed for 5 h, the solid were gradually dissolved and the color of solution slowly changed to yellowish brown with a trace amount of white precipitate. At the end of reaction, the solution was filtered to remove the white precipitate and 0.097 g (0.5 mmol) of $AgBF_4$ was added to the filtrate. After the mixture was stirred for 2 h at room temperature, it was filtered to remove AgCl and the volume of the filtrate was reduced to ca. 3 ml under vacuum. The concentrated solution was put in refrigerator overnight to form lots of orange microcrystals. The product was filtrated, washed with the mixture solution (1:2) of methanol and diethyl ether, and dried under vacuum to give 0.128 g (63%) orange microcrystals. Anal. Calc. for $C_{86}H_{76}B_2Cl_6F_8P_4Ru_2$: C, 56.69; H, 4.20. Found: C, 56.43; H, 4.17. ^1H NMR: δ (ppm) 4.58 (d, 8H), 5.30 (s, 12H), 6.56–7.60 (m, 52H). $^{31}P\{^1H\}$ NMR: δ (ppm) 38.82 (s). **3** could be also prepared by the reaction of **1** with BDNA under the same reaction conditions.

3.4. Crystallography

The crystals were grown from solvent mixtures of CH_2Cl_2, CH_3OH and Et_2O. They were covered with a thin layer of paraffin oil as a precaution against the possible decomposition in air, and mounted on a Rigaku RAXIS IIC imaging-plate diffractometer. Intensity data were collected using graphite-monochromatized Mo Kα ($\lambda = 0.71073$ 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. The crystal data and data refinements for complexes **1**, **2** and **3** were listed in Table 1.

4. Results and discussion

These complexes were obtained as air stable crystals. They were very soluble in CH_2Cl_2 and $CHCl_3$, partially soluble in benzene, toluene, and alcohol. Their solutions were air sensitive. In complex **1**, a singlet at 33.18 ppm in $^{31}P\{^1H\}$ NMR spectrum indicated that the two phosphorus atoms in the complex were equivalent. In ^1H NMR spectrum, a singlet at δ 3.49 ppm should be from the methylene protons in BDNA. The protons on the coordinated benzene ring showed a singlet at 5.35 ppm. Results of elemental analysis indicated that the complex was a binuclear compound containing two ruthenium atoms to share a BDNA (Scheme 2 **D**) and it was consistent with the results of X-ray diffraction of single crystal showed in Table 2, and Fig. 1.

If $[(\eta^6\text{-}C_6H_6)RuCl_2]_x$ complex was used as a starting materials, two metal atoms bridged by one diphosphine ligand was generally formed by using the diphosphine with the flexible backbone as a ligand, such as $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–4) [13,14]. However, $[(\eta^6\text{-}C_6H_6)RuCl_2]_x$ reacted with a rigid backbone diphosphine ligand, the diphosphine-bridged complex would be difficult to form and it was generally considered as a contaminating material or a side-product in the process of forming $[RuCl(\eta^6\text{-}C_6H_6)\text{-}(P\text{-}P)]^+$ (P-P = bidentate phosphine) [15]. Faraone [14] reported that the reaction of $\{(\eta^6\text{-}C_6H_6)RuCl_2[\mu\text{-}Ph_2P\text{-}(CH_2)_nPPh_2]RuCl(\eta^6\text{-}C_6H_6)_2\}$ with $Ph_2P(CH_2)_nPPh_2$ gave a mononuclear complex $\{(\eta^6\text{-}C_6H_6)RuCl\text{-}[Ph_2P(CH_2)_n\text{-}PPh_2]\}^+$ as the principal product. James [15] also described the similar results as Faraone's and thought that bridged species was an intermediate to form the cationic mononuclear complex $\{(\eta^6\text{-}C_6H_6)RuCl[Ph_2P(CH_2)_n\ PPh_2]\}^+$. However, $[(\eta^6\text{-}C_6H_6)RuCl_2(\mu\text{-BDNA})RuCl_2(\eta^6\text{-}C_6H_6)]$ did not further react with the diphosphine BDNA in methanol at room temperature. Complex **1** appeared to be very stable under this reaction condition. In spite of ruthenium and BDNA was mixed in the molar ratio of 1:1 and the reaction time was extended over 48 hours, the excess ligand did not react further with the binuclear complex **1** to form the monomeric complex $[RuCl(\eta^6\text{-}C_6H_6)(P\text{-}P)]Cl$. If the coordinated benzene was thought to be tridentate ligand, complex **1** had a stable structure of six coordination atoms. On the other hand, the rigid backbone of BDNA and the formation of a large 8-membered chelating ring would be unfavourable for the substitution of chloride with one phosphorus atom at room temperature. Yamamoto synthesized mononuclear $[(arene)RuCl(BDNA)]^+$ by reacting the coordination unsaturated $[(arene)RuCl]^+$ with BDNA [22].

The reactions of complex **1** with $AgBF_4$ give the complex **2** as the major product (Scheme 3). The data of

Table 1
Crystal data for complex **1**, **2** and **3**

Complexes	**1**	**2**	**3**
Empirical formula	$C_{48}H_{48}Cl_4O_3P_2Ru_2$	$C_{49}H_{46}BCl_3F_4OP_2Ru_2$	$C_{86}H_{76}B_2Cl_6F_8P_4Ru_2$
Formula weight	1078.74	1108.10	1821.81
Temperature (K)	296(2)	294(2)	294(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
Unit cell dimensions			
a (Å)	12.8100(11)	14.4981(18)	13.732(3)
b (Å)	21.507(2)	15.644(2)	14.351(3)
c (Å)	18.471(2)	20.788(3)	19.733(4)
α (°)	90	90	90
β (°)	107.950(4)	103.404(3)	94.82(3)
γ (°)	90	90	90
Volume (Å^3)	4841.1(7)	4586.6(10)	3875.0(13)
Z	4	4	2
Density (calculated) (Mg m^{-3})	1.480	1.0605	1.561
Absorption coefficient (mm^{-1})	0.949	0.957	0.746
F(000)	2184	2232	1848.00
Crystal size (mm)	$0.14 \times 0.12 \times 0.12$	$0.50 \times 0.16 \times 0.14$	$0.22 \times 0.20 \times 0.14$
θ range for data collection (°)	1.50–25.60	1.94–27.56	1.74–24.00
Limiting indices	$0 \leqslant h \leqslant 15$, $-25 \leqslant k \leqslant 25$, $-22 \leqslant l \leqslant 21$	$-18 \leqslant h \leqslant 14$, $-20 \leqslant k \leqslant 20$, $-26 \leqslant l \leqslant 26$	$-16 \leqslant h \leqslant 16$, $0 \leqslant k \leqslant 17$, $0 \leqslant l \leqslant 23$
Reflections collected	11 628	31 026	4372
Independent reflections (R_{int})	7072 (0.0479)	10 546 (0.0896)	4316 (0.0000)
Absorption correction	ABSCOR	Multi scans	Semi-empirical
Max. and min. transmission		1.00 and 0.72	1.000 and 0.844
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7052/0/542	10 546/21/557	4266/30/488
Goodness-of-fit on F^2	1.153	0.999	1.098
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0750$, $wR_2 = 0.1567$	$R_1 = 0.0553$, $wR_2 = 0.1222$	$R_1 = 0.0669$, $wR_2 = 0.1586$
R indices (all data)	$R_1 = 0.1157$, $wR_2 = 0.1823$	$R_1 = 0.1415$, $wR_2 = 0.1587$	$R_1 = 0.0933$, $wR_2 = 0.1881$
Extinction coefficient	0.00117(8)		0.00001(11)
Largest diff. peak and hole (e Å^{-3})	0.677 and −0.507	0.991 and −0.796	0.485 and −0.370

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

Ru(1)–C(51)	2.171(4)	Ru(1)–C(52)	2.180(4)	Ru(1)–C(53)	2.160(5)
Ru(1)–C(54)	2.169(4)	Ru(1)–C(55)	2.212(4)	Ru(1)–C(56)	2.237(4)
Ru(1)–Cl(1)	2.3998(10)	Ru(1)–Cl(2)	2.4191(10)	Ru(1)–P(1)	2.3449(8)
Ru(2)–C(61)	2.146(4)	Ru(2)–C(62)	2.164(4)	Ru(2)–C(63)	2.207(5)
Ru(2)–C(64)	2.235(4)	Ru(2)–C(65)	2.145(4)	Ru(2)–C(66)	2.154(4)
Ru(2)–Cl(3)	2.4035(10)	Ru(2)–P(2)	2.3568(9)	Ru(2)–Cl(4)	2.4071(9)
P(2)–Ru(2)–Cl(3)	87.46(3)	P(2)–Ru(2)–Cl(4)	84.71(3)	Cl(1)–Ru(1)–Cl(2)	87.49(3)
Cl(3)–Ru(2)–Cl(4)	87.40(3)	Cl(1)–Ru(1)–Cl(2)	87.49(3)		

NMR spectra and elemental analysis showed that only one chloride was dissociated by $AgBF_4$. Complex **1** bearing benzene ligand shows obviously the difference from the ruthenium complex containing other aromatic compounds, such as, pentamethylcyclopentadienyl and *p*-cymene in spite of the diphosphine is the same [22]. Even though the extension of the reactive time, the excess amount of silver ion does not result in the further dissociation of chlorides in the complex **2** to give a binuclear complex bridged by two chlorides such as [{(η^6-arene)Ru(μ-Cl)}$_2$(μ-BDNA)](OTf)$_2$ [22]. To our best knowledge, there has been no report about two ruthenium atoms are bridged by one chloride in η^6-arene-ruthenium complexes bearing bidentate phosphine bridge. Comparing with *p*-cymene and pentamethylcyclopentadienyl, the coordinated benzene in complex **2** does not contain any electron-donating group which causes the decrease of positive charge on ruthenium. The higher positive charge on complex **2** could suppress the further dissociation of chloride.

However, when the reaction of $(\eta^6\text{-}C_6H_6)RuCl_2]_x$ with BDNA was carried out in refluxing methanol, it was surprising to obtain a new 16-membered ring binuclear cationic complex $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-BDNA})_2RuCl(\eta^6\text{-}C_6H_6)]^{2+}$ as a main product (Scheme 4). Girolami and Toppioni reported the analogous complexes bearing the substituted cyclopentadienyl and diphosphines, but they were

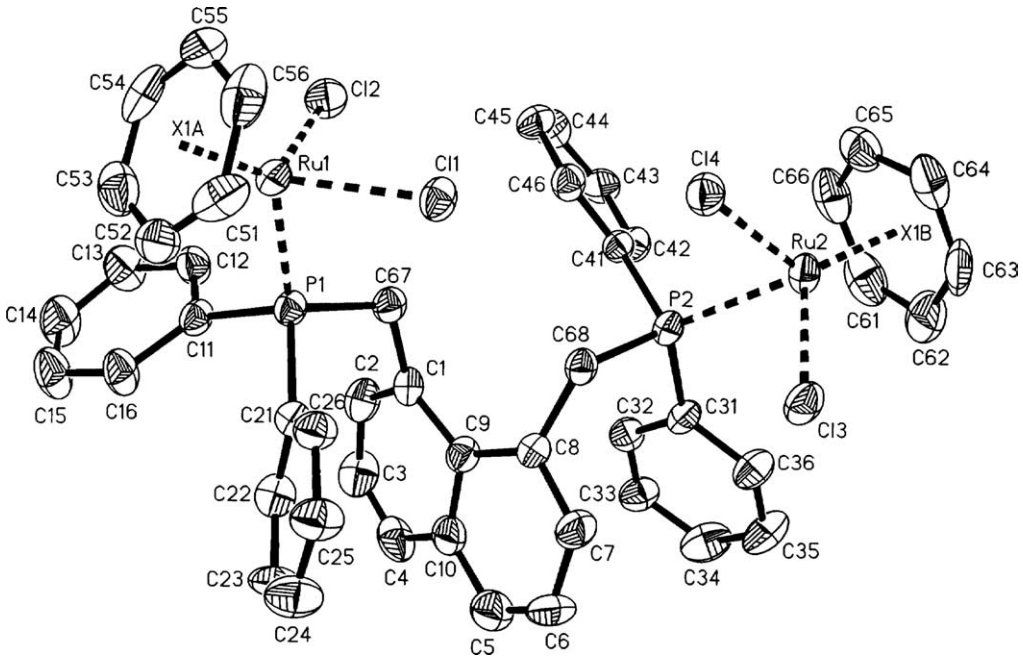
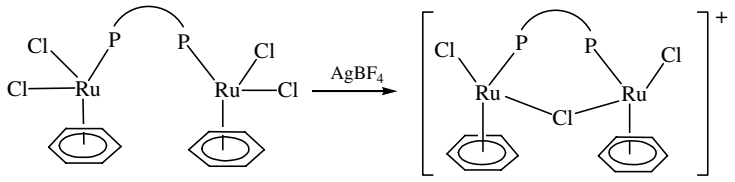
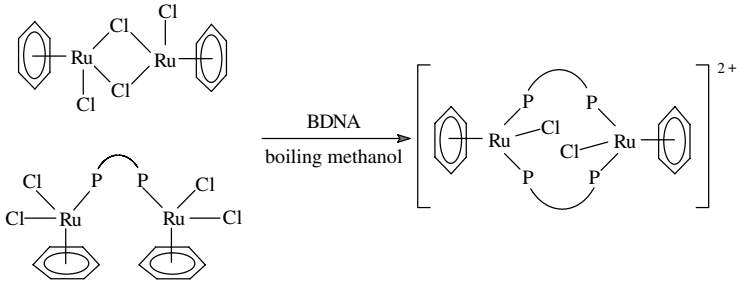


Fig. 1. An ORTEP drawing of complex **1**.



Scheme 3.



Scheme 4.

only consisted of a 8-membered and 10-membered rings, and the crystal structure data of these complexes did not report [16,21]. Similarly, if equimolar of $[(\eta^6\text{-}C_6H_6)\text{-}RuCl_2(\mu\text{-BDNA})RuCl_2(\eta^6\text{-}C_6H_6)]$ and BDNA were refluxed in methanol, the same cyclic binuclear complex $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-BDNA})_2RuCl(\eta^6\text{-}C_6H_6)]^{2+}$ was also formed as a major product. The formation of the large 16-membered ring complex should result from the unique structure of BDNA being of a large rigid backbone. If BDNA chelates one ruthenium atom, a unstable 8-membered chelating ring will be formed. At room temperature, two phosphorus atoms of BDNA can cause the breaking of the chloride-bridged bond in $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ to generate complex **1** and the excess of BDNA cannot further react with complex **1**. However, when the reaction was carried at refluxing methanol, the higher reaction temperature promoted chloride substitution by one phosphorus atom in BDNA. In order to effectively decrease the tension of the chelating ring, the complex **3** was formed by two BDNA ligands bridging two ruthenium atoms rather than one BDNA chelating one metal atom.

An ORTEP drawing of the complex **1** determined by X-ray diffraction was shown in Fig. 1. Each ruthenium atom in the complex was comprised of a η^6-bound benzene and it had pseudo-octahedral geometry defined by two chlorides, one phosphorus of BDNA and a tridentate benzene

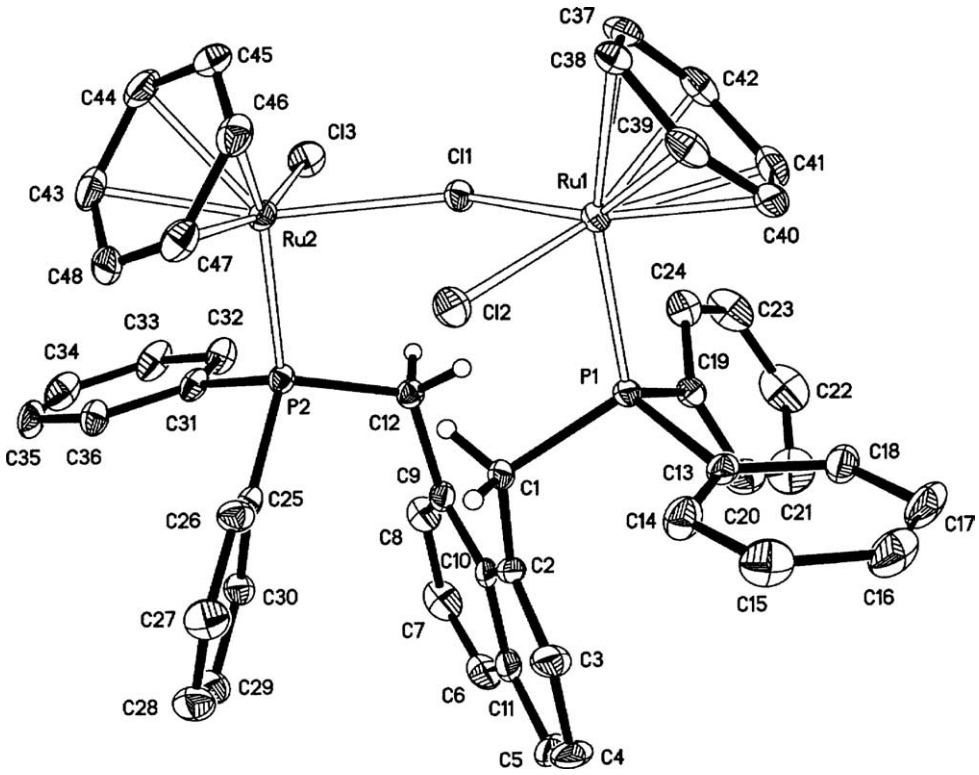


Fig. 2. An ORTEP drawing of complex **2**.

ligand. The binuclear complex molecule had a C_2-axis passing through C_9 and C_{10}. The bond lengths of Ru(1)–P(1) 2.3449 Å was slightly different from Ru(2)–P(2) 2.3569 Å, but they were almost the same as Ru–P(1) 2.379 Å and Ru–P(2) 2.334 Å in monomeric complex $\{RuCl(C_6H_6)$-[(*S*)-BINAP]$\}^+$ [5], were slightly longer bond lengths than Ru–P 2.34 Å in $[(HMB)RuCl_2]_2$(μ-DMPE) [19,20] [HMB, hexamethylbenzene; DMPE, 1,3-bis(dimethylphosphino)propane] and Ru–P 2.318(3) Å in $[\{CpRu(CH_3CN)_2\}_2$-(dppe)$]^{2+}$ [22]. They were also very close to the bond length in some mononuclear complexes, such as 2.359 Å in $\{RuCl_2$(*p*-cymene)$[P(CH_2C_6H_5)_3]\}$ [31].

The ORTEP drawing of complex **2**, and the selected bond length and angles of complex **2** were given in Fig. 2 and in Table 3, respectively. In this complex, the two η^6-C_6H_6 planes are arranged in the *trans* position. The molecule possesses C_2 symmetry axial. The bond lengths of bridged chloride to Ru(1) and Ru(2) are 2.4328 and 2.4713 Å. They are close to Ru(1)–Cl(1) and Ru(1)–Cl(1)* 2.439(3) and 2.459(3) Å in $[\{$(*p*-cymene)Ru(μ-Cl)$\}_2$(μ-BDNA)$](OTf)_2$ bridged by two chlorides [22]. Ru(1)–P(1) 2.3520(9) Å, Ru(2)–P(2) 2.3827(10) Å are little shorter than Ru(1)–P(1) 2.396(3) Å in $[\{$(*p*-cymene)Ru(μ-Cl)$\}_2$(μ-BDNA)$](OTf)_2$, and also close to corresponding bond lengths in complex **1**. The bond angle Ru(1)–Cl(1)–Ru(2) 133.64(4) Å is much larger than Ru(1)–Cl(1)–Ru(1)* 98.56(9) Å in $[\{$(*p*-cymene)Ru(μ-Cl)$\}_2$(μ-BDNA)]-$(OTf)_2$.

The crystal structure of complex **3** was shown in Fig. 3. According to the ORTEP drawing, Ru(1) coordination structure was the same as in Ru(1A), the dinuclear molecule had a C_2 symmetric axial through C(41) and C(41A). If the coordinated benzene ring was thought to be tridentate coordination, each ruthenium and its coordinated atoms formed a slightly distorted octahedron. The selected bond lengths and angles in Table 4 showed the

Table 3
Selected bond lengths and bond angles of complex **2**

Ru(1)–P(1)	2.3520(9)	Ru(1)–Cl(2)	2.3932(9)
Ru(1)–Cl(1)	2.4328(10)	Ru(2)–P(2)	2.3827(10)
Ru(2)–Cl(3)	2.3851(10)	Ru(2)–Cl(1)	2.4713(9)
P(1)–C(19)	1.811(3)	P(1)–C(13)	1.819(4)
P(1)–C(1)	1.837(3)	P(2)–C(25)	1.838(3)
P(2)–C(31)	1.841(4)	P(2)–C(12)	1.850(3)
C(39)–Ru(1)–P(1)	122.74(11)	C(41)–Ru(1)–P(1)	91.40(11)
C(40)–Ru(1)–P(1)	94.42(10)	C(42)–Ru(1)–P(1)	115.17(11)
C(37)–Ru(1)–P(1)	152.57(10)	C(38)–Ru(1)–P(1)	159.97(11)
C(39)–Ru(1)–Cl(2)	88.21(10)	C(41)–Ru(1)–Cl(2)	149.75(12)
P(1)–Ru(1)–Cl(2)	86.38(3)	P(1)–Ru(1)–Cl(1)	88.19(3)
Cl(2)–Ru(1)–Cl(1)	90.53(3)	C(43)–Ru(2)–P(2)	103.64(6)
C(48)–Ru(2)–P(2)	91.61(11)	C(44)–Ru(2)–P(2)	136.29(12)
P(2)–Ru(2)–Cl(1)	91.95(3)	Cl(3)–Ru(2)–Cl(1)	81.28(3)
Ru(1)–Cl(1)–Ru(2)	133.64(4)	C(19)–P(1)–C(13)	106.49(15)
C(19)–P(1)–C(1)	106.00(16)	C(13)–P(1)–C(1)	106.96(15)
C(19)–P(1)–Ru(1)	116.06(5)	C(13)–P(1)–Ru(1)	106.91(11)
C(1)–P(1)–Ru(1)	113.86(11)	C(25)–P(2)–C(12)	105.68(15)
C(31)–P(2)–Ru(2)	109.67(12)	C(12)–P(2)–Ru(2)	112.24(11)
C(2)–C(1)–P(1)	117.2(2)	C(14)–C(13)–P(1)	120.50(3)
C(18)–C(13)–P(1)	120.2(3)	C(24)–C(19)–P(1)	120.9(3)
C(20)–C(19)–P(1)	121.4(3)	C(26)–C(25)–P(2)	121.8(3)
C(30)–C(25)–P(2)	119.8(3)	C(32)–C(31)–P(2)	123.3(3)
C(36)–C(31)–P(2)	117.4(3)		

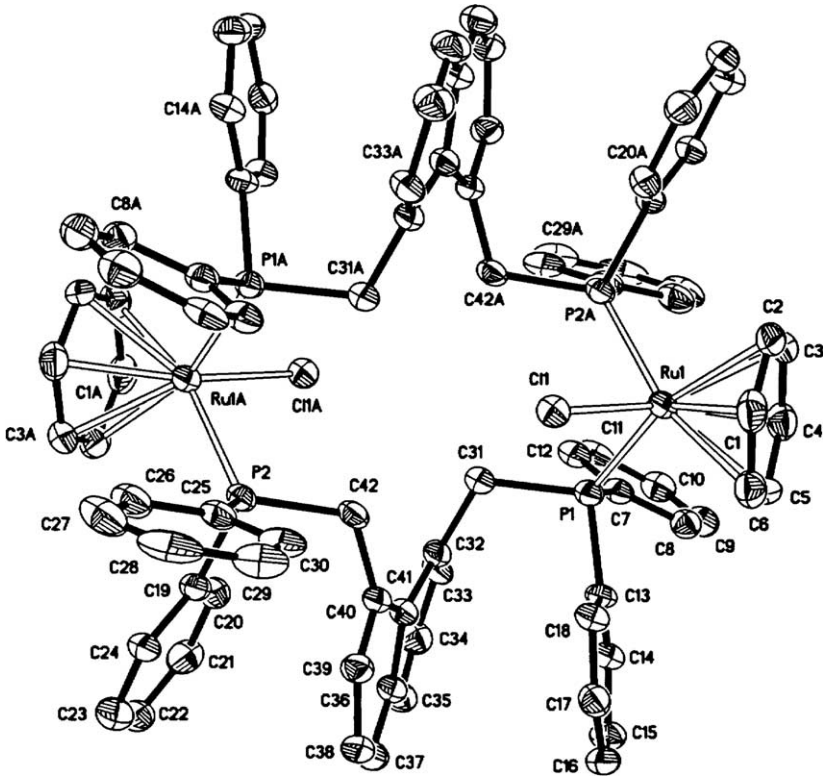


Fig. 3. ORTEP drawing of complex **3**.

Table 4
Selected bond lengths and bond angles of complex **3**

Ru(1)–C(3)	2.201(2)	Ru(1)–C(4)	2.214(2)
Ru(1)–C(5)	2.233(2)	Ru(1)–C(1)	2.259(2)
Ru(1)–C(2)	2.261(2)	Ru(1)–C(6)	2.264(2)
Ru(1)–P(1)	2.3471(8)	Ru(1)–P(2)	2.3767(9)
Ru(1)–Cl	2.385		
C(3)–Ru(1)–C(4)	36.83(6)	C(3)–Ru(1)–C(5)	65.36(8)
C(4)–Ru(1)–C(5)	36.57(6)	C(3)–Ru(1)–C(1)	65.27
C(3)–Ru(1)–C(2)	36.36(5)	C(4)–Ru(1)–C(2)	65.72(7)
C(5)–Ru(1)–C(2)	76.30(8)	C(1)–Ru(1)–C(2)	35.88(6)
C(3)–Ru(1)–C(6)	77.26(8)	C(4)–Ru(1)–C(6)	65.92(7)
C(5)–Ru(1)–C(6)	36.14(5)	C(1)–Ru(1)–C(6)	35.95(6)
C(2)–Ru(1)–C(6)	64.70(8)	C(3)–Ru(1)–P(1)	131.40(5)
C(4)–Ru(1)–P(1)	98.05(5)	C(5)–Ru(1)–P(1)	86.56(6)
C(1)–Ru(1)–P(1)	137.55(5)	C(2)–Ru(1)–P(1)	162.41(6)
C(6)–Ru(1)–P(1)	103.35(5)	C(3)–Ru(1)–P(2)	89.56(6)
C(4)–Ru(1)–P(2)	109.60(5)	C(5)–Ru(1)–P(2)	145.30(4)
C(1)–Ru(1)–P(2)	127.73(5)	C(2)–Ru(1)–P(2)	97.98(6)
C(6)–Ru(1)–P(2)	162.61(5)	P(1)–Ru(1)–P(2)	93.86(3)
C(3)–Ru(1)–Cl(1)	139.54(4)	C(4)–RU(1)–Cl(1)	159.88(6)
C(5)–Ru(1)–Cl(1)	126.14(4)	C(1)–Ru(1)–Cl(1)	84.52(6)
C(2)–Ru(1)–Cl(1)	104.17(5)	C(6)–Ru(1)–Cl(1)	94.16(5)
C(2)–Ru(1)–Cl(1)	104.17(5)	C(6)–Ru(1)–Cl(1)	94.16(5)
P(1)–Ru(1)–Cl(1)	89.04(3)	P(2)–Ru(1)–Cl(1)	88.54(3)

bond lengths of Ru(1)–P(1) 2.3471 Å, Ru(1)–P(2) 2.3767 Å, Ru(1)–Cl(1) 2.385 Å, and Ru(1)–C (in coordinated benzene ring) 2.239 Å (average) were very close to Ru–P(1) 2.334 Å, Ru–P(2) 2.379 Å, Ru–Cl 2.393 Å, and Ru–C 2.273 Å (average) in $[(\eta^6\text{-}C_6H_6)RuCl(BINAP)]^+$ [5], Ru–P(1) 2.353 Å and Ru–P(2) 2.381 Å in $[(\eta^6\text{–}p\text{-cymene})RuCl(DPPF)]^+$ [17], and also very close to Ru(1)–P(1) 2.345, Ru(2)–P(2) 2.357 Å Ru–C 2.188 Å (average) in $[(\eta^6\text{-}C_6H_6)RuCl_2(\mu\text{-BDNA})RuCl_2(\eta^6\text{-}C_6H_6)]$. The bond angles of P(1)–Ru(1)–Cl(1) and P(2)–Ru(1)–Cl(1) were 89.04° and 88.54°, respectively. The bond angle of P(1)–Ru(1)–P(2) 93.86° was very close to 93.6° in $[(\eta^6\text{-}p\text{-cymene})\text{-}RuCl(DPPF)]^+$, and slightly larger than 91.4° in $[(\eta^6\text{-}C_6H_6)RuCl(BINAP)]^+$.

5. Conclusion

The complexes formed by the reacting of 1,8-bis(diphenylphosphinomethyl)naphthalene with $[(\eta^6\text{-}C_6H_6)RuCl_2]_x$ show some unique characters in structure. The structure characters of complexes **2** and **3** in the η^6-benzene ruthenium complexes bearing bidentate phosphine ligands are originally discovered and determined by the diffraction of single crystal. The research on catalytic properties of the complexes is progressing.

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