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Synthesis and characterization of ruthenium complexes of 1,8-bis(diphenylphosphinomethyl)naphthalene (BDNA) and their catalytic hydrogenation reactions to α,β-unsaturated aldehydes

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Abstract

A new ligand BDNA [1,8-bis(diphenylphosphinomethyl)naphthalene] and three ruthenium complexes containing the new ligand, $Ru_2Cl_4(BDNA)_2$ **1**, $RuHCl(CO)(PPh_3)(BDNA)$ **2**, and $RuH_2(CO)(PPh_3)(BDNA)$ **3**, have been synthesized. Their compositions and structures were characterized by $^{31}P\{^1H\}$-NMR, ^1H-NMR, and elemental analysis. Molecular structure of **3** was also confirmed by single-crystal X-ray diffraction. The crystal belonged to the triclinic crystal system, $P\bar{1}$ space group, $a = 10.7450(7)$, $b = 12.7100(7)$, $c = 18.1390(13)$ Å, $\alpha = 89.558(6)$, $\beta = 83.117(2)$, $\gamma = 80.859(5)°$, $V = 2428.0(3)$ Å^3, and $Z = 2$. The hydrogenation results of citral and cinnamaldehyde revealed that complex **2** had good catalytic activity and complex **3** had the high selectivity for the hydrogenation of C=O bond in α,β-unsaturated aldehydes to form the corresponding allylic alcohols. In the presence of complex **3,** very high selectivities of 99.5 and 95.1% were obtained for the hydrogenation of the carbonyl group in citral and cinnamaldehyde, respectively.

Keywords: Ruthenium complex; 1,8-Bis(diphenylphosphinomethyl)naphthalene; Hydrogenation; Citral; Cinnamaldehyde

1. Introduction

The syntheses and catalytic reaction of platinum group metal complexes have been one of the most active research areas because they generally exhibit excellent hydrogenation properties for unsaturated organic compounds [1–5]. A number of neutral ruthenium complexes of tertiary phosphine, hydride and carbonyl ligands, such as, $RuCl_2(PPh_3)_3$ [6], $RuHCl(CO)(PPh_3)_3$ [7] and $RuH_2(CO)(PPh_3)_3$ [8] are excellent catalysts and their hydrogenation mechanisms have also been extensively investigated. In general, bidentate phosphine ligand will have better capability to control the coordination number, stoichiometry and stereochemistry of the resulting complex than the monodentate phosphine ligand. Bidentate phosphine complexes could enhance better catalytic activity and selectivity in comparison to the monodentate phosphine complexes [9,10], especially, in asymmetric catalysis [11–15]. α,β-Unsaturated aldehydes are valuable intermediates in the field of fragrance and flavor chemistry, and they are also often involved in the tedious syntheses of novel fine chemical products [16]. The selective reduction of carbonyl group conjugated with the C=C bond is still a challenging problem, and only a few reports have been published on the selective formation of unsaturated alcohols by using boron and aluminum hydride as reducing agents [17,18] or catalyzed by transition metal complexes with primary or secondary alcohols serving

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as hydrogen donors [19–22]. Catalytic hydrogenation appears to be the most attractive way to carry out these reductions, when economic and industrial processing factors are taken into consideration, but results with high activity and selectivity are still scarce [23,24]. In the previous paper [9], we have reported that ruthenium complexes bearing a BISBI [2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl] ligand had very good catalytic hydrogenation activity for citral and cinnamaldehyde and adequate hydrogenation selectivity to form the corresponding allylic alcohols. In this paper, we would like to report the synthesis of BDNA, a new bidentate phosphine ligand, and three novel ruthenium complexes bearing the new BDNA ligand, $Ru_2Cl_4(BDNA)_2$, $RuHCl(CO)(PPh_3)(BDNA)$ and $RuH_2(CO)(PPh_3)(BDNA)$. Initial results have shown that these complexes were much better catalysts for the selective hydrogenation of C=O bond in α,β-unsaturated aldehydes than the analogous ruthenium complexes of PPh_3 or BISBI.

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. Reagent-grade PPh_3 and 1,8-di(bromomethyl)naphthalene were purchased from Aldrich, citral (97%) and cinnamaldehyde (98%) from Riedel-deHaen and they were distilled before use. $RuCl_3 \cdot xH_2O$ ($>42\%$ Ru) was purchased from Kunming Nobel Metals, China. Starting materials $RuCl_2(PPh_3)_3$ [25], $RuHCl(CO)(PPh_3)_3$ [26] and $RuH_2(CO)(PPh_3)_3$ [26] were prepared according to the reported methods.

2.2. Analytical methods

The ^{1}H- and ^{31}P{^{1}H}-NMR spectra were recorded on a Bruker DPX 400 spectrometer at room temperature (r.t.), 400.13 MHz for ^{1}H and 160.97 MHz for ^{31}P. The chemical shifts of ^{31}P{^{1}H}-NMR were relative to 85% H_3PO_4 as external standard, ^{1}H-NMR relative to TMS as internal standard, with downfield shifts as positive. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. FTIR was recorded on a Perkin Elmer 1600 spectrometer with a KBr plate.

2.3. Catalytic hydrogenation

An appropriate amount of catalyst and substrate solution were introduced into a stainless steel autoclave (100 ml) equipped with a stirrer (Parr 4561 minireactor). The autoclave was evacuated and flushed with high purity hydrogen five times, consecutively, and was filled with hydrogen to the reaction pressure. After the reaction solution was heated to the desired temperature, the stirrer was started (400 rpm) and the reaction time was noted. The reaction was quenched by immersing

Table 1
Experimental data for the X-ray diffraction studies

Empirical formula	$C_{55}H_{51}O_3P_3Ru$
Formula weight	953.94
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.7450(7)
b (Å)	12.7100(7)
c (Å)	18.1390(13)
α (°)	89.558(6)
β (°)	83.117(2)
γ (°)	80.859(5)
Volume (Å^3), Z	2428.0(3), 2
$D_{calc.}$ (g cm^{-3})	1.305
Absorption coefficient (mm^{-1})	0.464
F (000)	988
Crystal size (mm)	$0.30 \times 0.24 \times 0.15$
θ range for data collection (°)	1.13–25.00
Limiting indices	$-13 \le h \le 12$, $-15 \le k \le 0$, $-22 \le l \le 21$
Reflections collected	7286
Independent reflections	7286 ($R_{int} = 0.0000$)
Absorption correction	Abscor
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7236/0/560
Goodness-of-fit on F^2	0.704
Final R indices [$I > 2\sigma$ (I)]	$R_1 = 0.0787$, $wR_2 = 0.2191$
R indices (all data)	$R_1 = 0.0855$, $wR_2 = 0.2564$
Extinction coefficient	0.0108 (8)
Largest difference peak and hole (e Å^{-3})	1.205 and −1.750

Table 2
Selected bond lengths and angles for $RuH_2(CO)(PPh_3)(BDNA)$

Bond length (Å)	
Ru–P(1)	2.3236(6)
Ru–P(2)	2.3688(6)
Ru–P(3)	2.3014(6)
Ru–C(63)	1.8291(2)
Bond angle (°)	
C(63)–Ru–P(3)	76.71(8)
C(63)–Ru–P(1)	100.25(7)
P(3)–Ru–P(1)	154.22(2)
C(63)–Ru–P(2)	97.24(7)
P(3)–Ru–P(2)	95.56(2)
P(1)–Ru–P(2)	101.36(2)
C(58)–C(59)–C(62)	114.9(3)
C(60)–C(59)–C(62)	126.0(2)
C(52)–C(51)–C(61)	113.2(3)
C(60)–C(51)–C(61)	126.5(2)

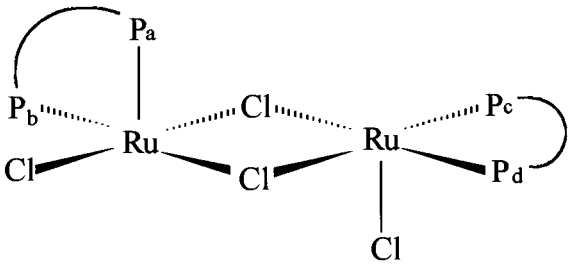


Fig. 1. Proposed structure of complex **1**.

the reactor in an ice bath at the end of the hydrogenation. The products were analyzed on GC (Hewlett-Packard (HP) 5890 series II) with an FID and a capillary column (HP-FFAP, 25 m × 0.2 mm × 0.33 μm), and the GC graphs were obtained with a HP 3396 integrator. The components were identified by authentic sample on GC and GC–MS (HP 5890 GC with a series mass selective detector).

3. Preparation of ligand and complexes

3.1. Preparation of 1,8-bis(diphenylphosphinomethyl)naphthalene (BDNA)

Triphenylphosphine 3.6 g (13.7 mmol) and lithium 0.3 g (43.2 mmol) in 25 ml THF were stirred for 3 hours at r.t., and the orange–red solution was filtered to remove the unreacted lithium. *t*-Butylchloride 1.25 g (13.5 mmol) in 10 ml THF was dropped slowly into the filtrate which was cooled using an ice-bath. At the end of addition, the solution was heated to reflux for 10 min. After the solution was cooled to 0°C, 1,8-di(bromomethyl)naphthalene 2.0 g (6.4 mmol) in 20 ml THF was dropped slowly into the cooled solution over a period of 30 min. During the addition of 1,8-dibromomethylnaphthalene, the reaction mixture changed to a pale orange color with the formation of white microcrystalline precipitates. The reaction mixture was heated to reflux for 30 min before the solvent was evaporated under vacuum to give a yellowish orange sticky solid. CH_2Cl_2 (50 ml) and water (20 ml) were added to dissolve the solid mixture, and then the mixture was separated in a separatory funnel. The organic layer was collected and reduced to about 20 ml under vacuum. Addition of 30 ml ethanol to the CH_2Cl_2 solution caused the formation of white needle crystals. The product was filtered, washed with ethanol, and dried under vacuum for 2 h to give 2.4 g (72%) of BDNA as white needles. M.p.: 226–228°C (in air) with decomposition. Anal. Calc. for $C_{36}H_{30}P_2$: C, 82.27; H, 5.76. Found: C, 82.15; H, 5.64%. $^{31}P\{^1H\}$-NMR: δ (ppm) −10.8 (s); ^{1}H-NMR: δ (ppm) 4.22 (4H, s), 6.64–7.66 (26 H, m).

3.2. $Ru_2Cl_4(BDNA)_2$ **1**

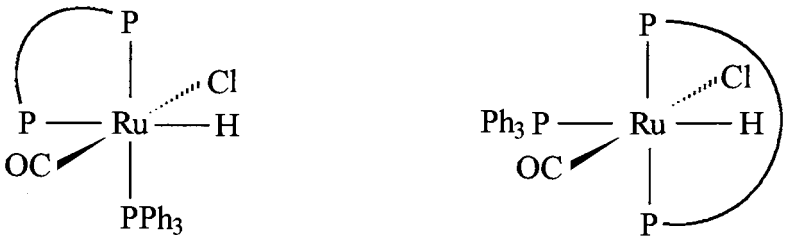
$RuCl_2(PPh_3)_3$ 0.48 g (0.5 mmol) and BDNA 0.26 g (0.5 mmol) were suspended in 20 ml acetone. After the mixture was heated to reflux for 1 h, the reaction mixture changed to dark brown color with the formation of orange–red precipitates. Then, the mixture was cooled to r.t. and the product was filtered, washed with diethyl ether, and dried under vacuum to give 0.34 g (80%) yield of **1** as orange–red powder. Anal. Calc. for $C_{72}H_{60}Cl_4P_4Ru_2$: C, 63.49; H, 4.44. Found: C, 63.14; H, 4.56%. $^{31}P\{^1H\}$-NMR spectrum: δ(ppm) P_A 61.89 (d), P_B 55.75 (d) with $J_{AB} = 47.1$ Hz; P_c 43.03 (d), P_d 49.87 (d) with $J_{CD} = 31.5$ Hz.

3.3. $RuHCl(CO)(PPh_3)(BDNA)$ **2**

$RuHCl(CO)(PPh_3)_3$ 0.190 g (0.2 mmol) and BDNA 0.105 g (0.2 mmol) were dissolved in 10 ml toluene. The solution was refluxed for 3 h. During reflux, the color of the solution was slowly changed to pale yellow. At the end of reaction, 20 ml *n*-hexane was added, then the solution was kept in refrigerator overnight to form microcrystalline white needles. The product was filtered, washed with diethyl ether and dried under vacuum to give 0.14 g (85%) of **2** as white needles. Anal. Calc. for $C_{55}H_{46}ClOP_3Ru$: C, 69.36; H, 4.87. Found: C, 69.29; H, 4.93%. FTIR: $\nu_{CO} = 1934.0$ cm^{-1} (vs). ^{1}H-NMR and $^{31}P\{^1H\}$-NMR had two sets of peaks with the intensity ratio of ca. 3:1. ^{1}H-NMR peaks of the major complex was centered at δ (ppm) −6.44 (ddd) with $J_{H-P_{cis}} = 17.4$, 17.4 Hz and $J_{H-P_{trans}} = 112.5$ Hz, and the minor complex was centered at δ (ppm) −6.78 (ddd) with $J_{H-P_{cis}} = 20.4$, 20.6 Hz and $J_{H-P_{trans}} = 111.0$ Hz. $^{31}P\{^1H\}$-NMR of the major complex had peaks at δ (ppm) 51.82 (dd), 37.98 (dd) and 27.03 (dd) with $J_{P-P_{cis}} = 18.9$, 18.8 Hz and $J_{P-P_{trans}} = 292.8$ Hz, the minor complex had peaks at δ (ppm) 37.90 (dd), 31.78 (dd) and 6.12 (t) with $J_{P-P_{cis}} = 12.7$ Hz and $J_{P-P_{trans}} = 297.6$ Hz.

3.4. $RuH_2(CO)(PPh_3)(BDNA)$ **3**

$RuH_2(CO)(PPh_3)_3$ 0.183 g (0.2 mmol) and BDNA 0.105 g (0.2 mmol) dissolved in 10 ml toluene was refluxed for 3 h. During reflux, the solution color changed slowly to pale yellow. At the end of the reaction, 20 ml *n*-hexane was added, then the solution was kept in refrigerator overnight to form white microcrystals. The product was filtered, washed with diethyl ether and dried under vacuum to give 0.12 g (72%) of **3** as white microcrystals. Anal. Calc. for $C_{55}H_{47}OP_3Ru \cdot 2H_2O$: C, 69.24; H, 5.39. Found: C, 69.21; H, 5.23%. IR: $\nu_{CO} = 1953.3$ cm^{-1}. $^{31}P\{^1H\}$- and ^{1}H-NMR were similar to those of the complex **2**. ^{1}H-NMR: *trans*-isomer, δ (ppm) −7.35 (dddd) with



A B

Fig. 2. Proposed structures of complex **2**.

$J_{H_a-P_{cis}} = 35.6$ Hz, $J_{H_a-P_{trans}} = 61.1$ Hz, and $J_{H_a-H_b} = 11.0$ Hz; and -8.24 (dddd) with $J_{H_b-P_{cis}} = 36.3$ Hz, $J_{H_b-P_{trans}} = 125.4$ Hz; *cis*-isomer, the peaks could not be clearly identified because of the overlapping with the hydride peaks of the *trans*-isomer. $^{31}P\{^1H\}$-NMR: *trans*-isomer: δ (ppm) 56.8 (ddd) and 49.8 (t) with $J_{P-P_{cis}} = 17.5$ Hz and $J_{P-P_{trans}} = 183.8$ Hz; *cis*-isomer: δ (ppm) 61.4 (d) and 46.3 (t) with $J_{P-P} = 17.0$ Hz.

3.5. X-ray crystallographic analysis of $RuH_2(CO)(PPh_3)(BDNA)$ **3**

The crystal used for X-ray diffraction was prepared from a 1:1 solvent mixture of dichloromethane and *n*-hexane. The colorless prism crystal was mounted on a MSC/Rigaku PAXIS IIC imagine-plate diffractometer. Intensity data were collected at 294 K using graphite-monochromatized Mo–K_α ($\lambda = 0.71073$ Å) radiation from a rotating-anode generator operating at 50 kV and 90 mA (taking 53 oscillation photos in the range 0–159°, exposure 8 min per frame). A self-consistent semi-empirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied using the ABSCOR program. All calculations were performed with Siemens SHELXTL PLUS (PC Version) system. Structure refinement was based on F^2 for all 7236 reflections. A final *R*-factor was 0.0787, *wR* 0.2191, the largest and mean Δ/σ, and the largest difference peaks are presented in Table 1. Table 2 contains selected bond distances and angles.

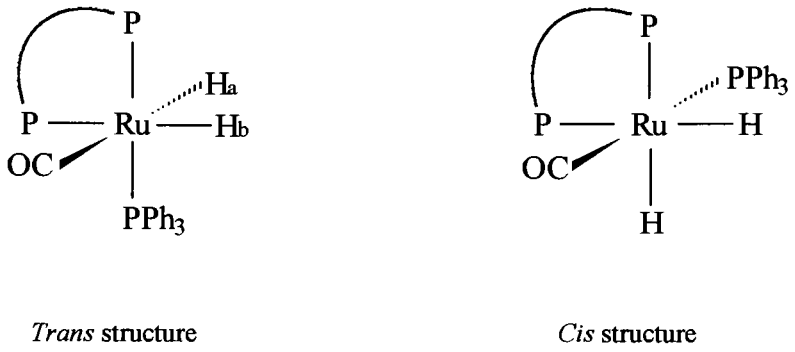
4. Results and discussion

4.1. The BDNA ligand

There are several reported routes for the synthesis of di-*t*-phosphines [27–29]. In the present study, reaction of alkali metal diphosphide with dibromide in THF was chosen because it was a convenient route with satisfactory yield. The ligand BDNA was not very soluble in THF, therefore, a lot of crystalline solid product appeared during the addition of 1,8-di(bromomethyl)naphthalene. BDNA has shown good solubility in CH_2Cl_2 and $CHCl_3$ but was only sparingly soluble in alcohol. The ligand was very sensitive to air oxidation in organic solution although the dry white needle crystals appeared to be quite stable in air.

4.2. Complex **1**

The orange–red complex was not very stable either in solution or in solid form. When the complex was dissolved in organic solvent, such as toluene or dichloromethane, the color of the solution was orange under nitrogen atmosphere. If the solution was exposed to air, the orange color would change to green color within a few minutes. However, the orange–red powder of complex **1** was more stable to air oxidation, the color change could only be observed after exposing to air for 24 h. Our original plan was to synthesize $RuCl_2(PPh_3)(BDNA)$ by ligand exchange of $RuCl_2(PPh_3)_3$ with BDNA. Unexpectedly, the $^{31}P\{^1H\}$-NMR spectrum showed two doublets of doublets with equal intensities and elemental analyses also agreed with the dinuclear structure of $Ru_2Cl_4(BDNA)_2$. The structural differences of the ligands have obviously influenced the formation of the target complexes and their properties. In our previous study [9], when BISBI was used as ligand, only the desired product $RuCl_2(PPh_3)(BISBI)$ was isolated under similar preparation conditions. Although the PPh_3 in the complex $RuCl_2(PPh_3)(BISBI)$ would completely dissociate in benzene or chloroform to form the dimer complex $[RuCl_2(BISBI)]_2$ in solution, only the original mononuclear complex $RuCl_2(PPh_3)(BISBI)$ could be crystallized from the organic solution when we attempted to isolate the dimer complex. Basset et al. have also reported similar observation for the reaction of $RuCl_2(PPh_3)_3$ and TPPTS [trisodium salt of the tri(*m*-sulfophenyl)phosphine] to form the dimer complex $[RuCl_2TPPTS_2]_2$ owing to the large cone angle of TPPTS (ca. 170 vs. 145° for PPh_3) [30]. To the best of our knowledge, it is very unusual to observe that a



Trans structure *Cis* structure

Fig. 3. Proposed structures of complex **3**.

dinuclear complex could be generated in high yield with equilmolar amounts of $RuCl_2(PPh_3)_3$ and a bidentate phosphine ligand. According to the $^{31}P\{^1H\}$-NMR spectrum, the structure of the dinuclear complex was proposed as shown in Fig. 1. In order to ensure the dinuclei structure of the complex, measurement of molecular weight by vapor pressure osmometer would be helpful in future studies.

4.3. Complex **2**

It was prepared by the ligands exchange of $RuHCl(CO)(PPh_3)_3$ with BDNA in refluxing toluene. The solid state complex as well as its organic solution were quite stable to air oxidation. However, the yellow organic solution would gradually change to dark brown color after it had been exposed to air for 2 days. The carbonyl absorption peak was very strong and had overlapped with the Ru–H bond absorption of complex **2** in the IR spectrum. ^{1}H-NMR spectra of the hydride in the complex showed two sets of doublets of double doublet peaks with similar splitting pattern. The intensity ratio of the two sets of peaks was ca. 3:1. $^{31}P\{^1H\}$-NMR also showed two sets of peaks. The results have suggested that the product was a mixture containing two kinds of structures. According to the splitting pattern of peaks and the coupling constants, all phosphorus atoms in the two isomers were arranged in meridional forms and the hydrides in the two isomers were in the *trans*-position to one of the phosphorus atoms. Therefore, the hydride in the major isomer was in *trans* position of a phosphorus atom of BDNA (Fig. 2 **A**), but the hydride in the minor isomer was in *trans* position of triphenylphosphine (Fig. 2 **B**). The amount of the former isomer was about three time higher than the latter isomer. The two phosphorus atoms of BDNA in the latter configuration were not equal because the rigid backbone of BDNA had caused the complex to form a distorted octahedron. The conclusion was also supported by the doublets of double doublets of the hydride in ^{1}H-NMR spectrum.

4.4. Complex **3**

The colorless microcrystalline product was prepared by a similar method as complex **2** and it was stable in air. If the organic solution of the complex was exposed to air, it would slowly decompose to brownish color after two days. The absorption peak of Ru–H in complex **3** could not be clearly identified in the IR spectrum because of the very strong carbonyl peak overlapping with the weak Ru–H absorption. The ^{1}H-NMR spectra showed two sets of peaks, one had much higher intensity than the other with the intensity ratio of ca. 10:1. The strong peaks appeared as two doublets of doublets of double doublets at -7.35 and -8.25 ppm, and the weak peaks were shown as two octets at -7.95 and -8.70 ppm. The $^{31}P\{^1H\}$-NMR spectra also displayed two sets of peaks, and the intensity ratio of the two sets were also ca. 10:1. The strong peaks appeared as a doublet of double doublets at 56.7 ppm and a triplet at 49.8 ppm, and the weak peaks appeared as a doublet at 61.3 ppm and a triplet at 46.2 ppm. These NMR spectra have strongly indicated that the stronger peaks were from the the *trans*-isomer, and the weaker peaks were from the *cis*-isomer. The proposed structures of the two isomeric complexes are shown in Fig. 3.

The results of single-crystal X-ray diffraction were listed in Tables 1 and 2 and Fig. 4. They were in agreement with the proposed *trans*-structure as shown in Fig. 3. According to the X-ray diffraction results, a crystal cell contained four water molecules. Ru–P(3) and Ru–P(1) were in *trans*-positions to each other and the steric barrier was less than Ru–P(2) in the middle position, so the bond lengths were shorter than Ru–P(2). The same phenomenon was also observed in the analogous complex of BISBI [9]. The phosphorus atoms of the bidentate phosphine ligand occupied the *trans*-position because of the flexible backbone and larger chelating ring of the bidentate phosphine ligand in the BISBI complex. The rigid backbone of BDNA restricted the bidentate phosphine ligand to coordinate

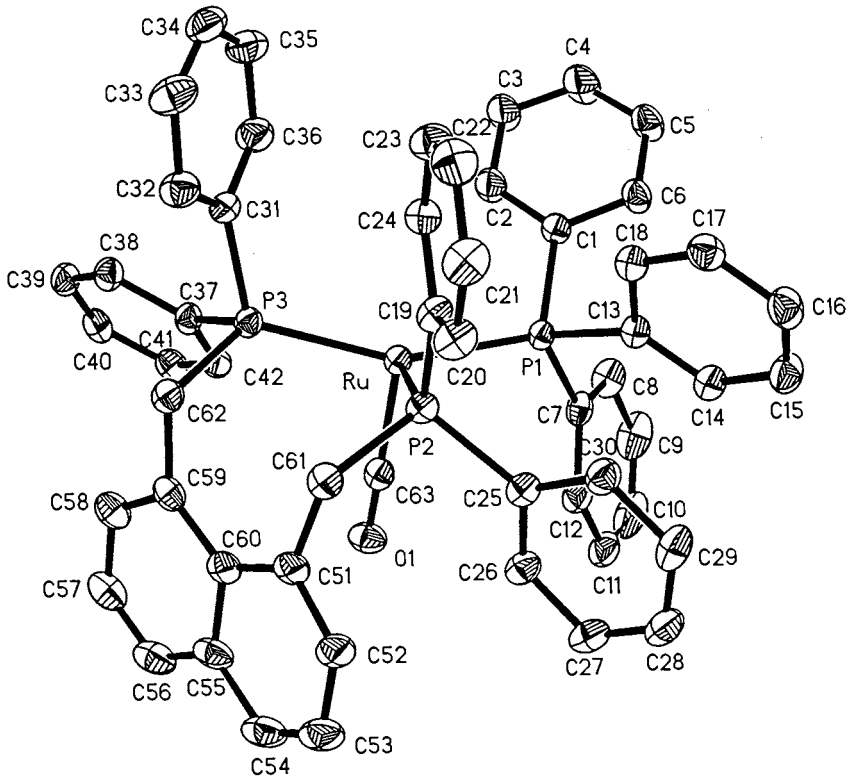


Fig. 4. ORTEP drawing of complex **3**.

in *cis*-position, and created a large distorted force in the chelating ring, and resulted in that the bond angles of P(1)–Ru–P(2), C(60)–C(59)–C(62) and C(60)–C(51)–C(61) were much larger than those of P(2)–Ru–P(3), C(58)–C(59)–C(62) and C(52)–C(51)–C(61), respectively. Although the hydrides were not located in the structure, it was reasonable to believe that they occupied the *trans*-positions of CO and P(2).

*4.5. Hydrogenation of citral and cinnamaldehyde catalyzed by ruthenium complexes **1–3***

Hydrogenation results of citral and cinnamaldehyde are summarized in Table 3. The substitution of PPh_3 by BDNA had significantly improved the selectivities of ruthenium complexes **1–3** for the hydrogenation of C=O bond in α,β-unsaturated aldehydes to form allylic

Table 3
Hydrogenation of α,β-unsaturated aldehydes

Catalyst	Citral[a]		Cinnamaldehyde[b]	
	Conversion (%)	Selectivity[c] (%)	Conversion (%)	Selectivity[c] (%)
$RuCl_2(PPh_3)_3$	35.4	35.8	39.7	61.5
$Ru_2Cl_4(BDNA)_2$	15.5	92.3	13.6	86.8
$RuHCl(CO)(PPh_3)_3$	11.4	65.6	10.8	67.6
$RuHCl(CO)(PPh_3)(BDNA)$	92.7	95.5	86.4	93.9
$RuH_2(CO)(PPh_3)_3$	4.3	89.7	8.8	70.7
$RuH_2(CO)(PPh_3)(BDNA)$	63.8	99.5	61.5	95.1

Reaction conditions: toluene: 8.0 ml, substrates: 2.0 ml, catalyst conc.: 1.0×10^{-3} M, H_2 pressure: 50 kg cm^{-2}, time: 3 h.
[a] Reaction temperature: 80°C.
[b] Reaction temperature: 70°C.
[c] Selectivity in allylic alcohol.

alcohols. Although the catalytic activity of **1** was lower than the analogous PPh_3 complex, complexes **2** and **3** have shown much higher catalytic activities and selectivities for the formation of allylic alcohols than their analogues PPh_3 complexes. For example, the selectivity of **2** for the hydrogenation of C=O in citral was 95.5% (92.7% conversion) and the selectivity of **3** was 99.5% (63.8% conversion). Complex **2** had the highest catalytic activity and complex **3** showed the highest selectivity among the three complexes. These results have followed the same trend as the analogous ruthenium complexes containing BISBI described in our previous study [9]. The chemical environment of the phosphorus atoms in the BDNA ligand appeared to be very similar to the phosphorus atoms in the BISBI ligand. The immense difference of hydrogenation activity and selectivity between BISBI and BDNA complexes might originate from their different backbone structures, i.e., they were mainly controlled by steric factor and not electronic factor. The rigid structure of BDNA backbone and the large chelating ring in these complexes could play an important role for the significant improvement of hydrogenation selectivity. The IR spectra results have shown that the absorption of carbonyl group in complex **3** appeared at a higher wavenumber (ν_{CO} = 1953.3 cm^{-1}) than complex **2** (ν_{CO} = 1934.0 cm^{-1}) after the chloride in **2** was substituted by the hydride. This means that the electronic density of ruthenium in **2** was higher than in **3** which was in good agreement with the observed higher catalytic activity of **2** than **3** for the hydrogenation of α,β-unsaturated aldehydes.

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