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Coordination chemistry and catalytic activity of ruthenium(II) complexes containing a phospha-macrocyclic ligand

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Dedicated to Alfred Werner on the 100th Anniversary of his Nobel prize in Chemistry in 1913.

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ABSTRACT

Substitution of $[RuCl_2(CO)_3(THF)]$, $[RuCl_2(dmso)_4]$ and $[RuCl_2(PPh_3)_3]$ with a macrocyclic ligand, 2,3,4,5,6,7,8,9-octahydro-1,9-diphenyl-1*H*-5,1,9-benzazadiphosphacyclo undecine (**11-P_2NH**), provided [Ru(**11-P_2NH**)$Cl_2(CO)$] (**3**), [Ru(**11-P_2NH**)Cl_2(dmso)] (**4**) and [Ru(**11-P_2NH**)$Cl_2(CH_3CN)$] (**5**), respectively. These complexes were characterized by elemental analyses as well as NMR spectroscopy. The structure of **3** was further confirmed by X-ray diffraction analysis. The octahedral geometry around the ruthenium center is in agreement with the Werner's "coordination" bonding concepts. The chelate rings of the macrocycle toward Ru(II) center adopting into chair conformations were revealed. Furthermore, these ruthenium complexes were found to be active for *N*-alkylation of dibenzylamine with alcohols.

1. Introduction

Multidentate macrocyclic ligands represent an important class of direct extension of Werner's chelating ligands in coordination chemistry [1–4]. Among this context, phospha-macrocycles exhibit strong binding behavior toward transition metal ions [5–26]. Moreover, by suitable modification of donor atoms in the macrocyclic ligands, coordination behavior and geometry can be controlled [1–26]. For example, in the macrocycles **11-P_2X** which have a soft donor, i.e. phosphorus, sulfur or arsenic as shown in Chart 1, the **X** position was found to readily react with $W(CO)_6$ to yield tridentate facial complexes. In contrast, only the bidentate complexes were formed when **X** was a hard donor such as oxygen or nitrogen [14]. Ciampolini and coworkers also found that the stereochemistry at phosphorus centers can influence the coordination behavior of the metal ions [25,26]. In their findings, the macrocycle β-**18-P_4O_2** behaved as a tetra-dentate ligand toward cobalt(II) ions, whereas γ-**18-P_4O_2**, acting as a hexadenate, reacted with Co(II) ions to yield $[(\gamma\text{-}\mathbf{18\text{-}P_4O_2})Co]^{2+}$ [25].

As part of our research project on the coordinating capability of multi-dentate toward transition metal ions, we have reported the coordination chemistry of a phospha-macrocycle **11-P_2NH** toward $[FeCp(CO)_2Cl]$ (Scheme 1), resulting in **1**. The amine moiety of the macrocycle in **1** could be slowly converted into a coordinating imine [24]. Continuing our interest in this context, we explore the coordination chemistry of **11-P_2NH** toward Ru(II) and the catalytic activity of the resulting complexes.

2. Experimental

2.1. Methods and materials

All reactions, manipulations and purifications steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane and acetonitrile were dried over CaH_2 and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used after degassed process. Ligand **11-P_2NH** was prepared accordingly to the method reported previously [15].

Nuclear magnetic resonance spectra were recorded on a Bruker AVANCE 400 spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for ^1H and ^{13}C NMR, and relative 85% H_3PO_4 for ^{31}P NMR. Infrared spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series-II).

2.2. Synthesis and characterization

2.2.1. Complex *3*

A mixture of **11-P_2NH** (101 mg, 0.26 mmol) and $RuCl_2(CO)_3$(THF) (85 mg, 0.26 mmol) in THF (2 mL) was heated at refluxing temperature for 12 h. During the reaction, light yellow precipitates formed. Upon filtration, the solid product was washed with trace amount of THF and re-crystallized from CH_2Cl_2 and methanol to

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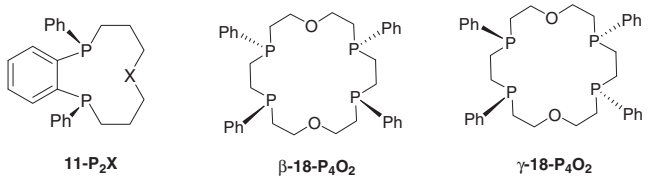
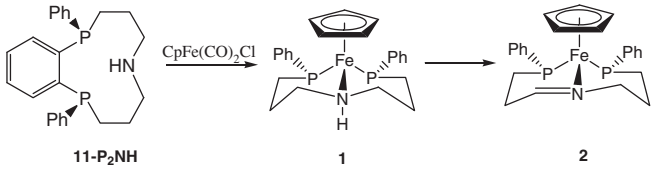


Chart 1. Various phospha-macrocycles.



Scheme 1. .

yield white crystalline solids (117 mg, 76%): IR (KBr): 1984 cm^{-1} (υ_{CO}); ^1H NMR (400 MHz, d_6-DMSO): δ 8.05–7.26 (m, 14H, Ar *H*), 3.99 (s, 1H, N*H*–), 3.49 (t, J = 7 Hz, 2H, –C*H*–),3.10–1.34 (m, 10H, –C*H*–); ^{13}C NMR (100 MHz): δ 199.8 (s, *C*O), 144.1 (m), 133.3, 133.1 (t, J_{C-P} = 8.7 Hz), 132.2 (d, J_{C-P} = 8.7 Hz), 131.3, 129.8 (d, J_{C-P} = 11.8 Hz), 129.5 (t, J_{C-P} = 5.5 Hz), 52.3. 25.1, 22.8; ^{31}P NMR (161 MHz, $CDCl_3$): δ 69.2.:ESI-MS *m/z*: 556.19 ([M−Cl]$^+$, calc. for $C_{25}H_{27}ClNOP_2Ru$: 556.03). Anal. Calc. for $C_{25}H_{27}Cl_2NOP_2Ru$: C, 50.77; H, 4.60; N, 2.37. Found: C, 50.54; H, 4.45; N, 2.07%.

2.2.2. Complex ***4***

A mixture of **11-P_2NH** (103 mg, 0.27 mmol) and $RuCl_2(dmso)_4$ (130 mg, 0.27 mmol) in THF (2 mL) was heated at refluxing temperature for 12 h. Upon filtration, the crude product was obtained as light yellow solids. Re-crystallization from THF/methanol gave light yellow solids (141 mg, 82%): ^1H NMR (400 MHz, $CDCl_3$): δ 7.80–7.33 (m, 14H, Ar *H*), 4.29 (s, 1H, N*H*–), 4.00 (m, 2H, –C*H*–), 2.83 (m, 2H, –C*H*–), 2.59 (m, 2H, –C*H*–), 2.44 (m, 2H, –C*H*–), 2.11 (s, 6H,dmso), 1.97 (m, 2H, –C*H*–), 1.39 (m, 2H, –C*H*–); ^{13}C NMR (100 MHz): δ 144.9 (t, J_{C-P} = 23.0 Hz), 134.6 (m), 133.3, 131.0 (t, J_{C-P} = 8.4 Hz), 130.8, 129.9, 127.6 (t, J_{C-P} = 4.5 Hz), 55.4, 46.0, 29.5, 24.1; ^{31}P NMR (161 MHz, $CDCl_3$): δ 72.5. ESI-MS *m/z*: 606.22 ([M−Cl]$^+$, calcd. for $C_{26}H_{33}ClNOP_2RuS$: 606.05). *Anal.* Calc. for $C_{26}H_{33}Cl_2NOP_2RuS$: C, 48.68; H, 5.18; N, 2.18. Found: C, 48.28; H, 5.01; N, 1.89%.

2.2.3. Complex ***5***

A mixture of **11-P_2NH** (99 mg, 0.26 mmol) and $RuCl_2(PPh_3)_3$ (249 mg, 0.26 mmol) in CH_3CN (2 mL) was heated at refluxing temperature for 12 h. During the reaction, light yellow solids precipitated. Upon filtration, the desired product was obtained as light yellow solids, which was then washed with THF (0.5 mL) and ether (0.5 mL). (117 mg, 76%): ^1H NMR (400 MHz, $CDCl_3$): δ 7.88–7.24 (m, 14H, Ar *H*), 3.86 (s, 1H, N*H*–), 3.58 (m, 2H, –C*H*–), 2.99 (m, 2H, –C*H*–), 2.65 (m, 2H, –C*H*–), 2.37–2.20 (m, 4H, –C*H*–), 1.40 (m, 2H, –C*H*–), 0.91 (s, 3H,C*H*$_3$CN); ^{13}C NMR (100 MHz): δ 143 (t, J_{C-P} = 24.0 Hz), 134.3, 133.1, 131.7 (t, J_{C-P} = 8 Hz), 131.0, 130, 127.6, 123.3, 54.3, 28.5 (m), 23.9, 4.8; ^{31}P NMR (161 MHz, $CDCl_3$): δ 81.8. ESI-MS *m/z*: 569.23 ([M−Cl]$^+$, calc. for $C_{26}H_{30}ClN_2P_2Ru$: 569.06). *Anal.* Calc. for $C_{26}H_{30}Cl_2N_2P_2Ru$: C, 51.66; H, 5.00; N, 4.63. Found: C, 51.37; H, 4.76; N, 4.38%.

2.2.4. Catalysis

Typical procedure for *N*-alkylation of dibenzylamine with an alcohol: a mixture of dibenzylamine (3.05×10^{-4} mol), catalysts (1∼2 mol % based on amine) and $NaBAr'_4$ in 3 eq. alcohol (9.15×10^{-4} mol) was placed in flask under the atmospheric pressure of nitrogen (or hydrogen) and was heated by an oil bath at 110–150 °C for a period of time. After the completion of the reaction, brine (3 mL) and CH_2Cl_2 (5 mL) were added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried over magnesium sulfate and concentrated. Products were characterized by NMR spectroscopy and the data were consistent with those reported. Product yields were obtained by the ^1H NMR integration compared to the internal standard. Spectral data of these compounds are essentially similar to those reported as listed below:

2.2.4.1. N,N-Dibenzyl(4-chlorobenzyl)amine. ^1H NMR (400 MHz, $CDCl_3$) δ 3.47 (s, 2H), 3.54 (s, 4H), 7.22–7.37 (m, 14H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 57.16, 57.87, 126.92, 128.23, 128.38, 128.65, 129.96, 132.44, 138.13, 139.36.

2.2.4.2. N,N-Dibenzyl(4-methylbenzyl)amine. ^1H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 3.44 (s, 2H), 3.46 (s, 4H), 7.08 (d, *J* = 7.6 Hz, 2H), 7.13–7.19 (m, 2H), 7.23–7.28 (m, 6H), 7.35–7.38 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 21.07, 57.56, 57.83, 126.75, 128.14, 128.66, 128.75, 128.86, 136.34, 136.45, 139.74.

2.2.4.3. N,N-Dibenzyl(4-methoxybenzyl)amine. ^1H NMR (400 MHz, $CDCl_3$) δ 3.41 (s, 2H), 3.45 (s, 4H), 3.73 (s, 3H, OC*H*$_3$), 6.82–6.87 (m, 2H), 7.11–7.21 (m, 2H), 7.27–7.32 (m, 6H), 7.31–7.41 (m, 4H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 57.5, 58.0, 58.2, 113.8, 126.9, 127.1, 128.3, 128.6, 129.0, 139.8, 158.6.

2.2.4.4. N,N-Dibenzyl(1-naphthalylmethyl)amine. ^1H NMR (400 MHz, $CDCl_3$) δ 3.54 (s, 4H), 3.64 (s, 2H), 7.14–7.18 (m, 2H), 7.23–7.28 (m, 4H), 7.35–7.46 (m, 6H), 7.47–7.53 (m, 1H), 7.73–7.76 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 57.93, 58.05, 125.47, 125.85, 126.84, 127.15, 127.36, 127.63, 127.85, 128.24, 128.73, 132.74, 133.33, 137.25, 139.59.

2.2.4.5. N,N-Dibenzyl-1-hexanamine. ^1H NMR (400 MHz, $CDCl_3$) δ 0.84, 1.26 (m, 11H), 2.42 (t, 2H), 3.54 (s, 4H), 7.26 (m, 10H).

2.2.4.6. N,N-Dibenzyl-3-phenylpropan-1-amine. ^1H NMR (400 MHz, $CDCl_3$) δ 1.74–1.87 (m, 2H), 2.46 (t, *J* = 7.1 Hz, 2H), 2.54 (t, *J* = 8.1 Hz, 2H), 3.54 (s, 2H), 7.08–7.19 (m, 3H), 7.15–7.38 (m, 12H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 29.04, 33.56, 52.93, 58.37, 125.58, 126.74, 128.13, 128.23, 128.37, 128.85, 139.83, 142.52.

2.3. X-ray crystallographic analysis

Crystals suitable for X-ray determination were obtained for **3** by recrystallization from CH_2Cl_2/MeOH at room temperature. Cell parameters were determined either by a Siemens SMART CCD diffractometer. Crystal data of these complexes are listed in Table 1. The structure was solved using the SHELXS-97 program [27] and refined using the SHELXL-97 program [28] by full-matrix least-squares on F^2 values.

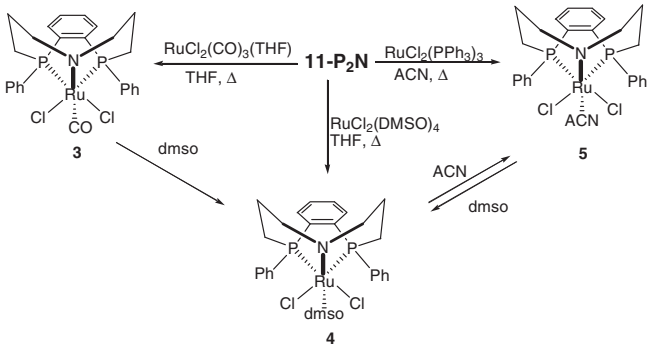
3. Results and discussion

3.1. Synthesis and characterization of ruthenium(II) complexes

The macrocyclic ligand **11-P_2NH** was prepared according to the previous reported methods [15]. A series of ruthenium(II) complexes containing **11-P_2NH** were prepared as shown in Scheme 2. Complexation of **11-P_2NH** with [$RuCl_2(CO)_3$(THF)], at a 1:1 ratio, under refluxing THF afforded a single substitution product of Ru(II) complex **3**. Treatment of **11-P_2NH** with equal molar amount of

Table 1
Crystal data of **3**.

Formula	$C_{25}H_{27}Cl_2NOP_2Ru$
Formula weight	591.39
Crystal system	orthorhombic
Space group	Pnma
a (Å)	10.6483(3)
b (Å)	18.3861(4)
c (Å)	12.9231(3)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3); Z	2530.09(11), 4
D_{calc} (Mg/m^3)	1.553
F(000)	1200
Crystal size (mm^3)	0.25 × 0.20 × 0.15
Reflections collected	15435
Independent reflections	2997(R_{int} = 0.0265)
θ range (°)	3.15–27.49
Refined method	Full-matrix least-squares on F^2
Goodness of fit on F^2	0.629
R indices [$I > 2\sigma(I)$]	$R1$ = 0.0248, $wR2$ = 0.0765
R indices (all data)	$R1$ = 0.0353, $wR2$ = 0.0832



Scheme 2. Complexation of **11-P_2NH** toward Ru(II) ions.

[$RuCl_2$(dmso)$_4$] [dmso:$(CH_3)_2$S=O] gave a ruthenium macrocyclic complex **4** in excellent yield. Similarly, substitution reaction of [$RuCl_2(PPh_3)_3$] with **11-P_2NH** generated the desired complex **5** in 76% yield. Furthermore, dissolving **3** in dimethylsulfoxide readily underwent the replacement of a dmso for a carbonyl to yield the complex **4**. Complex **4** was not converted back to **3** in the atmosphere of CO. However, complexes **4** and **5** are interconvertable to each other in suitable solvents (Scheme 2).

All complexes were obtained as yellow solids, which were characterized by elemental analysis, IR and NMR spectroscopy. The ^{31}P NMR spectra of **3**–**5** in $CDCl_3$ show only one resonance signal at δ 69.2, 72.5 and 81.8, respectively, indicating that both phosphorus donors of 11-P_2NH are bonded to the metal center in a symmetrical manner. Comparing with that of the free ligand 11-P_2NH, the ^{31}P resonance signals for all complexes are shifted down-field, in agreement with a metal-bound coordination shift. The IR spectrum for 3 shows a stretching frequency at 1984 cm^{-1}, corresponding to the terminal carbonyl ligand bound to the ruthenium ion. In addition, ^{13}C NMR resonance at 199.8 ppm also supports the existence of a Ru-CO moiety. ESI-MS of 3 shows a peak at m/z = 556.19 corresponding to the fragment of [3-Cl]$^+$. The molecular configuration of **3** is unequivocally confirmed by X-ray crystallographic analysis. (See Section 3.2).

As for the complex **4**, the observation of a singlet (δ 2.11 ppm) with integration of 6H in its ^{1}H NMR spectrum provides a convincing evidence for the coordination of dmso to the metal center, whereas the coordination of acetonitrile in 5 displays one set of methyl resonance at δ 0.91 ppm. ESI-MS spectra of **4** and **5** show

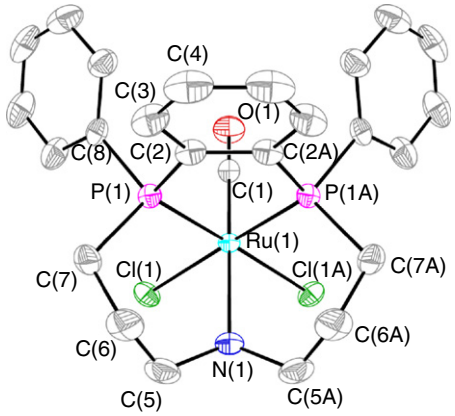


Fig. 1. ORTEP Plot of Complex **3** (Drawn with 30% probability ellipsoids).

Table 2
Selected bond distances (Å) and bond angles (°) of **3**.

Ru(1)–N(1)	2.230(2)	N(1)–Ru(1)–P(1)	94.42(7)
Ru(1)–P(1)	2.2428(6)	P(1)–Ru(1)–P(1A)	85.64(3)
Ru(1)–Cl(1)	2.4757(5)	C(1)–Ru(1)–N(1)	173.87(14)
Ru(1)–C(1)	1.849(3)	P(1)–Ru(1)–Cl(1A)	176.21(2)
C(1)–O(1)	1.135(4)	Cl(1)–Ru(1)–Cl(2)	89.02(3)

peaks at m/z = 606.22 [4-Cl]$^+$ and 569.23[5-Cl]$^+$, respectively. These observations well suggest the proposed structures for **4** and **5**.

3.2. X-ray structural analysis of complex *3*

The ORTEP plot of 3 is shown in Fig. 1, while some selected distances and angles are summarized in Table 2. The coordination sphere of the ruthenium metal is in slightly distorted octahedral geometry, with one face occupied by two chlorides and carbonyl and the other face by two phosphorus atoms and the nitrogen donor from the macrocyclic 11-P_2NH. This geometry around the ruthenium center is in agreement with the Werner's "coordination" bonding concepts [29]. The metal–ligand bond distances [Ru–P = 2.2428(6) and Ru–N = 2.230(2) Å] and bond angles [P(1)–Ru(1)–P(1A) = 85.64(3)° and P(l)–Ru–N(1) = 94.42(7)°] are all in the normal ranges for an O_h feature (Table 2). The macrocyclic conformation in 3 consists of one five- and two six-membered chelating rings. The five membered ring is attributed to *o*-phenylenebisphosphine-Ru, while both six-membered ones are constituted by Ru–N–C–C–C–P. Examination of those dihedral angles resulting from the ring [Ru–N(1)–C(5)–C(6)–C(7)–P(1)] reveals alternating + gauche/-gauche configuration of a typical chair form (Table 3). That deviation from the ideal 60° is due to the constraint of the bond lengths within the ring (e.g. Ru–P or Ru–N versus C–C).

3.3. Conformational analysis of complex *4* by NMR Spectroscopy

We were not able to acquire the crystal structures for complexes **4** and **5**. However, the conformational analysis of the six-

Table 3
Torsional angles for six-membered chelate rings for **3**.

P(1)–Ru(1)–N(1)–C(5)	31.8
Ru(1)–N(1)–C(5)–C(6)	−55.0
N(1)–C(5)–C(6)–C(7)	75.9
C(5)–C(6)–C(7)–P(1)	−70.3
C(6)–C(7)–P(1)–Ru(1)	48.6
C(7)–P(1)–Ru(1)–N(1)	−28.0

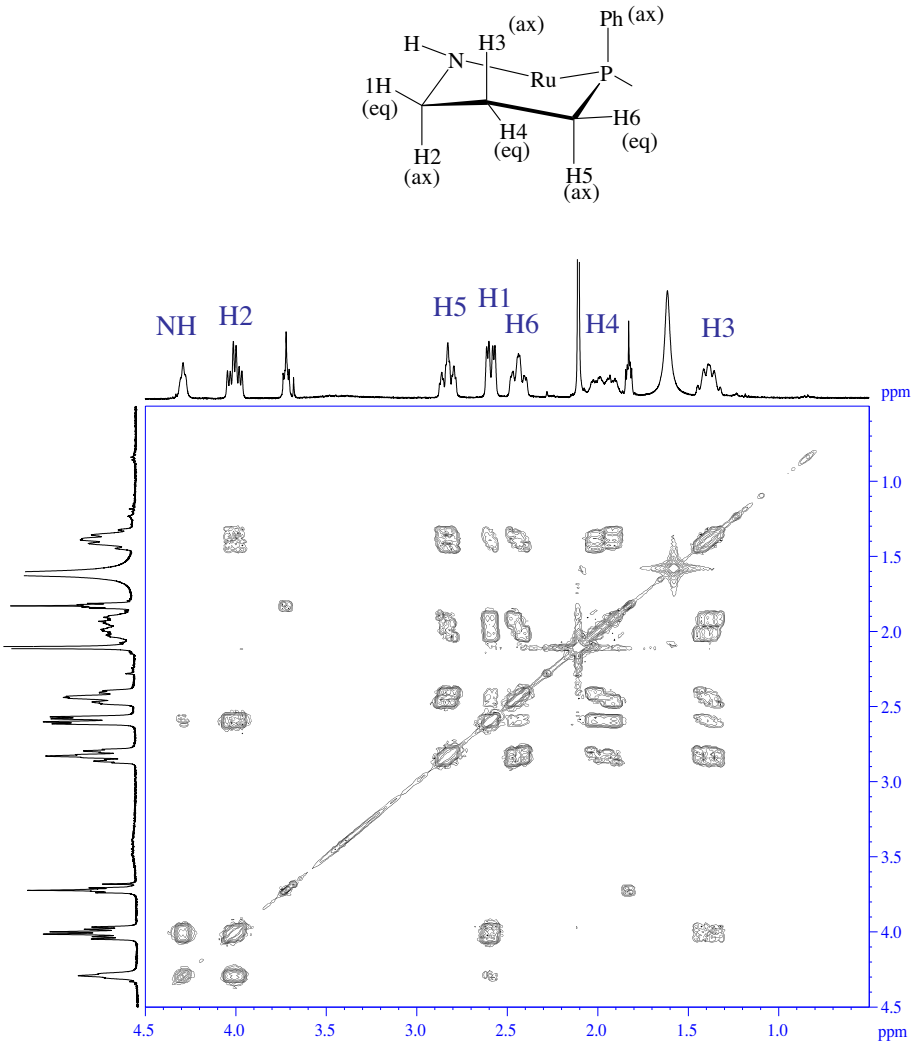


Fig. 2. COSY spectrum of **4**.

membered chelate ring may be achieved by the NMR analysis. The ^{1}H and ^{13}C signals assignments were based on the COSY and HSQC spectra. Fig. 2 shows the COSY spectrum of **4** in the region of 0–4.5 ppm. One can easily assign the chemical shift of each proton on the ring denoted as H1–H6, respectively, as indicated in the Fig. 2.

Both geminal and vicinal proton–proton coupling constants were determined by first-order approximation from the 400 MHz proton spectrum of 4 and are summarized in Table 4. The constants *J*(H2–H3) and *J*(H3–H5), which are substantially larger than 10 Hz, are considered to be affected by a dihedral angle close to 180°. The constants *J*(H1–H4), *J*(H4–H5) and *J*(H4–H6) are around 6 Hz, indicating the smaller dihedral angles among these C–H bonds. These results suggest that the six-membered chelate rings in **4** are in the chair conformations. Unlike complex **4**, the ill-resolved splitting patterns in **5** cause the determination for the coupling constants and conformation difficult.

Table 4
Coupling Constants of all protons in the six-membered chelate ring for **4**.[a]

Geminal coupling	Vicinal coupling[b]
J(H1∼H2) = 13.8	*J*(H1∼H4) = 5.9
J(H3∼H4) = 14.9	*J*(H2∼H3) = 14.3
J(H5∼H6) = 16.4	*J*(H3∼H5) = 13.8
	J(H4∼H5) = 5.8
	J(H4∼H6) = 5.6

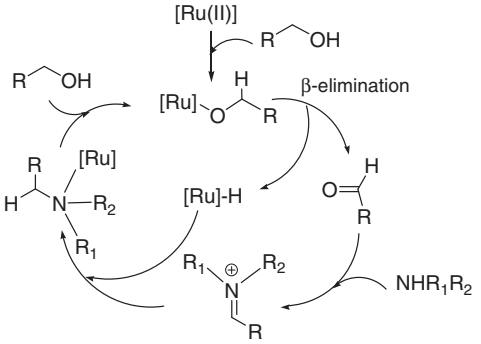
[a] In $CDCl_3$; in Hz.
[b] *J*(H2–H4), *J*(H1–H3), and *J*(H3–H6) are not able to be resolved.

3.4. Catalysis

It has been revealed that ruthenium complexes may serve suitable catalysts for *N*-alkylation of amines with alcohols, which involves a series of tandem reactions including oxidation of alcohols, condensation of amines with carbonyl compounds and reduction of imines as illustrated in Scheme 3 [30]. Thus we also investigated the catalytic activity of ruthenium complexes 3–5 toward *N*-alkylation of dibenzylamine with various alcohols. Under the typical reaction conditions commonly applied for the amination, the results of the coupling reaction of dibenzylamine with benzyl alcohol using various ruthenium complexes (Eq. (1)) are listed in Table 5.

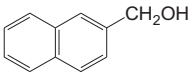
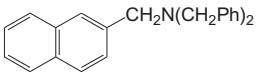
$$(PhCH_2)_2NH + PhCH_2OH \xrightarrow{[Ru]} (PhCH_2)_3N \quad (1)$$

The activities of the catalysts were substantially influenced by the ruthenium complexes and additives. A screening test suggested that carrying out the reaction at 110 °C with the use of ruthenium



Scheme 3. Catalytic pathway of Ru-catalyzed *N*-alkylation of amines with alcohols.

Table 6
N-alkylation of dibenzylamines with alcohols catalyzed by **3**.[a]

Entry	Alcohol	Product	Yield
1	*p*-$ClC_6H_4CH_2OH$	*p*-$ClC_6H_4N(CH_2Ph)_2$	100%
2	*p*-$MeC_6H_4CH_2OH$	*p*-$MeC_6H_4N(CH_2Ph)_2$	100%
3	*p*-$MeOC_6H_4CH_2OH$	*p*-$MeOC_6H_4N(CH_2Ph)_2$	100%
4			97%
5	$CH_3(CH_2)_5OH$	$CH_3(CH_2)_5N(CH_2Ph)_2$	33%
6	$C_6H_5(CH_2)_3OH$	$C_6H_5(CH_2)_3N(CH_2Ph)_2$	37%
7	$C_6H_5CH = CH_2CH_2OH$	$C_6H_5(CH_2)_3N(CH_2Ph)_2$	88%
8	$C_6H_5CH(OH)CH_3$	–	–

[a]Reaction conditions: dibenzylamine (3.05×10^{-4} mol), **3** (1 mol % based on amine) $NaBAr'_4$ (2 mol %) and benzyl alcohol (9.15×10^{-4} mol) at 110 °C for 24 h.

complexes containing phosphine-amine tridentates provided better yields of amine products evidenced by the entries 5, 6, 9 and 10 (Table 5). Among them, the ruthenium complex 3 with the macrocyclic 11-P2NH gives the best activity, indicating that the stabilization of the facial coordination mode of 11-P_2NH toward the metal center might play a crucial role on activity. Apparently, auxiliary ligands e.g. dmso versus CO, can also influence the activity (Table 5, entries: 6 versus 7 and 9 versus 11).

It has been known that the yields of amine products often increases as the reaction proceeds under ambient pressure of molecular hydrogen, presumably due to the acceleration of imine-reduction. However, in this study, the case of hydrogen is not necessary (Table 5, entries 7, 10, 14), suggesting that the *in situ* generated ruthenium hydrides ought to be active enough for the reduction of C=N bonds.

The reaction scope with respect to various alcohols was investigated (Table 6). Under the optimized reaction conditions, various substituted benzyl alcohol to yield the corresponding amines in excellent yields (Table 6, entries 1–4) except the secondary alcohol (Table 6, entry 8). Subjecting cinnamyl alcohol to the same conditions resulted in the formation of the product of C=C reduction, $C_6H_5CH_2CH_2CH_2N(CH_2C_6H_5)_2$ in high yield (88%), indicating the reduction of C=C bonds well competes with that of C=N bonds.

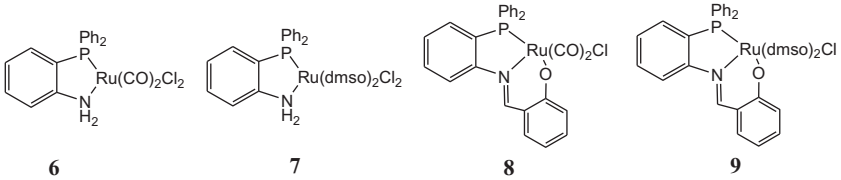
4. Summary

We have successfully prepared and structurally characterized a series of ruthenium complexes containing a macrocyclic ligand **11-P_2NH**. The structures of these complexes were unambiguously determined by spectroscopic methods as well as X-ray single crystal analysis for **3**. The *facial* coordination mode of **11-P_2NH** toward Ru(II) constitutes a macrocycle with the fuse of a five-membered and two six-membered chelate rings. The latter ones adopt into chair conformations. Unlike the known iron complex 1, the amine-donor in ruthenium complexes **3**–**5** does not undergo the oxidation to form the imine moiety. Complex **3** appears to be catalytically active for *N*-alkylation of dibenzylamine with various alcohols.

Table 5
Reductive amination catalyzed by Ru(II) complexes.[a]

Entry	[Ru] catalyst	Additive[b]	Temp. (°C)	Time	Yield[c]
1	**6** (1 mol%)[d]	–	110	24	trace
2	**6** (1 mol%)	$NaBAr'_4$	110	24	45%
3	**7** (1 mol%)[d]	$NaBAr'_4$	110	24	21%
4	**7** (1 mol%)	–	110	24	trace
5	**8** (1 mol%)[e]	$NaBAr'_4$	110	24	56%
6	**8** (2 mol%)	$NaBAr'_4$,	120	24	57%
7	**9** (1 mol%)[e]	$NaBAr'_4$, H_2 (1 atm)	110	24	24%
8	**3** (1 mol%)	-	110	24	43%
9	**3** (1 mol%)	$NaBAr'_4$,	110	24	67%
10	**3** (1 mol%)	$NaBAr'_4$, , H_2 (1 atm)	110	24	63%
11	**4** (1 mol%)	$NaBAr'_4$,	110	24	<10%
12	**4** (1 mol%)	$NaBAr'_4$,	150	24	35%
13	**5** (1 mol%)	$NaBAr'_4$	110	24	trace
14	**5** (1 mol%)	$NaBAr'_4$, H_2 (1 atm)	150	24	34%

[a]Reaction conditions: dibenzylamine (3.05×10^{-4} mol), catalysts (1–2 mol % based on amine), in 3 eq. benzyl alcohol (9.15×10^{-4} mol).
[b] $NaBAr'_4 = NaB[(3,5\text{-}(CF_3)_2C_6H_3)]_4$; 2 mol %.
[c] Yield based on ^1H NMR integration with mesitylene as the internal standard.
[d] Ref. [31].
[e] Ref. [32].



6 **7** **8** **9**

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Appendix A. Supplementary data

HSQC spectrum of **4**, COSY spectrum of **5,** tables of atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles are available. In addition, CCDC 880893 contains the supplementary crystallographic data for complex **3**. 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 http://dx.doi.org/10.1016/j.poly.2012.06.079.

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