Synthesis, Chemistry, and Catalytic Activity of Ruthenium Diaminodiphosphane Complexes − Crystal Structures of *trans*-[$RuCl_2\{\kappa^3$-$Ph_2PC_6H_4CH{=}NC_6H_{10}N(H)CH_2C_6H_4PPh_2\}(PPh_3)$] and *cis*-[$RuCl_2\{\kappa^4$-$Ph_2PC_6H_4CH{=}NC_6H_{10}N(H)CH_2C_6H_4PPh_2\}$]

Wai-Kwok Wong,*[a] Xiao-Ping Chen,[a] Wei-Xiong Pan,[b] Jian-Ping Guo,[a] and Wai-Yeung Wong[a]

Keywords: Ruthenium / N,P ligands / Catalysis / Oxidations

The interaction of [$RuCl_2(PPh_3)_3$] with one equivalent of *N*,*N'*-bis[2-(diphenylphosphanyl)benzyl]-1*R*,2*R*-cyclohexanediamine [1*R*,2*R*-P(NH)(NH)P] in dichloromethane at room temperature gave *trans*-[$RuCl_2\{\kappa^3$-1*R*,2*R*-P(NH)(NH)P}(PPh_3)] (**1**). When heated under reflux in toluene under a nitrogen atmosphere, **1** was converted into *trans*-[$RuCl_2\{\kappa^4$-1*R*,2*R*-P(NH)(NH)P}] (**2**). However, when **1** was stirred at room temperature in air, it was oxidized to *trans*-[$RuCl_2\{\kappa^3$-1*R*,2*R*-PN(NH)P}(PPh_3)] (**3**). Depending on the reaction conditions, **3** was converted into *trans*-[$RuCl_2\{\kappa^3$-1*R*,2*R*-P(NH)(NH)P=O}(PPh_3)] (**4**) when heated to 80 °C in toluene in air, to *cis*-[$RuCl_2\{\kappa^4$-1*R*,2*R*-PN(NH)P}] (**5**) when stirred at room temperature in acetone in air, or to *trans*-[$RuCl_2\{\kappa^4$-1*R*,2*R*-PN(NH)P}] (**6**) when heated under reflux in acetone under a nitrogen atmosphere. When heated under reflux in toluene under a nitrogen atmosphere, **5** isomerized to **6** quantitatively. When heated under reflux in mesitylene under a nitrogen atmosphere, **6** was slowly reduced to **2**. The solid state structures of **3** and **5** were ascertained by X-ray crystallography. Catalytic studies showed that **1** could catalyze the oxidation of alkanes and alkenes with molecular oxygen.

Introduction

Transition-metal complexes with chiral diamino-, diimino-, and diamidodiphosphane ligands have been shown to be effective catalysts for asymmetric hydrogen-transfer reactions,[1] epoxidations,[2] and allylic alkylations,[3−4] respectively. Thus, the synthesis of chiral diamino-, diimino-, and diamidodiphosphane ligands and their application as auxiliaries for the preparation of chiral catalysts have aroused considerable recent interest. We have investigated the preparation and chemistry of diamino-, diimino-, and diamidodiphosphane ligands,[5−10] and reported the synthesis of *N*,*N'*-bis[2-(diphenylphosphanyl)benzyl]-1*R*,2*R*-cyclohexanediamine [1*R*,2*R*-P(NH)(NH)P] and its Ru^{II},[7] Cu^{I}, and Ag^{I} complexes.[8] In this report, we describe the synthesis, reactivity, and catalytic activity of *trans*-[$RuCl_2\{\kappa^3$-1*R*,2*R*-P(NH)(NH)P}(PPh_3)] (**1**).

Results and Discussion

Unlike the reaction with [$RuCl_2(DMSO)_4$] in refluxing toluene, which gave the complex *trans*-[$RuCl_2\{\kappa^4$-1*R*,2*R*-P(NH)(NH)P}] (**2**),[7] 1*R*,2*R*-P(NH)(NH)P reacted with [$RuCl_2(PPh_3)_3$] in dichloromethane at room temperature to give *trans*-[$RuCl_2\{\kappa^3$-1*R*,2*R*-P(NH)(NH)P}(PPh_3)] (**1**), which was fully characterized by elemental analysis, NMR spectroscopy, and mass spectrometry. The ^{31}P NMR spectrum of **1** exhibited two doublets at $\delta = 48.6$ (d, $^2J_{PP} = 28.9$ Hz) and 38.9 (d, $^2J_{PP} = 28.9$ Hz) for the coordinated P atom of the P(NH)(NH)P ligand and PPh_3, respectively, and a singlet at $\delta = -13.3$ (s) for the dangling P atom of the P(NH)(NH)P ligand. The positive FAB mass spectrum of **1** showed a peak corresponding to its molecular ion $[M]^+$ at $m/z = 1096$ for ^{102}Ru and ^{35}Cl. The tridentate nature of the P(NH)(NH)P ligand was also confirmed by X-ray crystallography. While this work was in progress, the synthesis and structure of **1** appeared in the literature.[11] Our structural and spectroscopic data of **1** agree with the literature data.

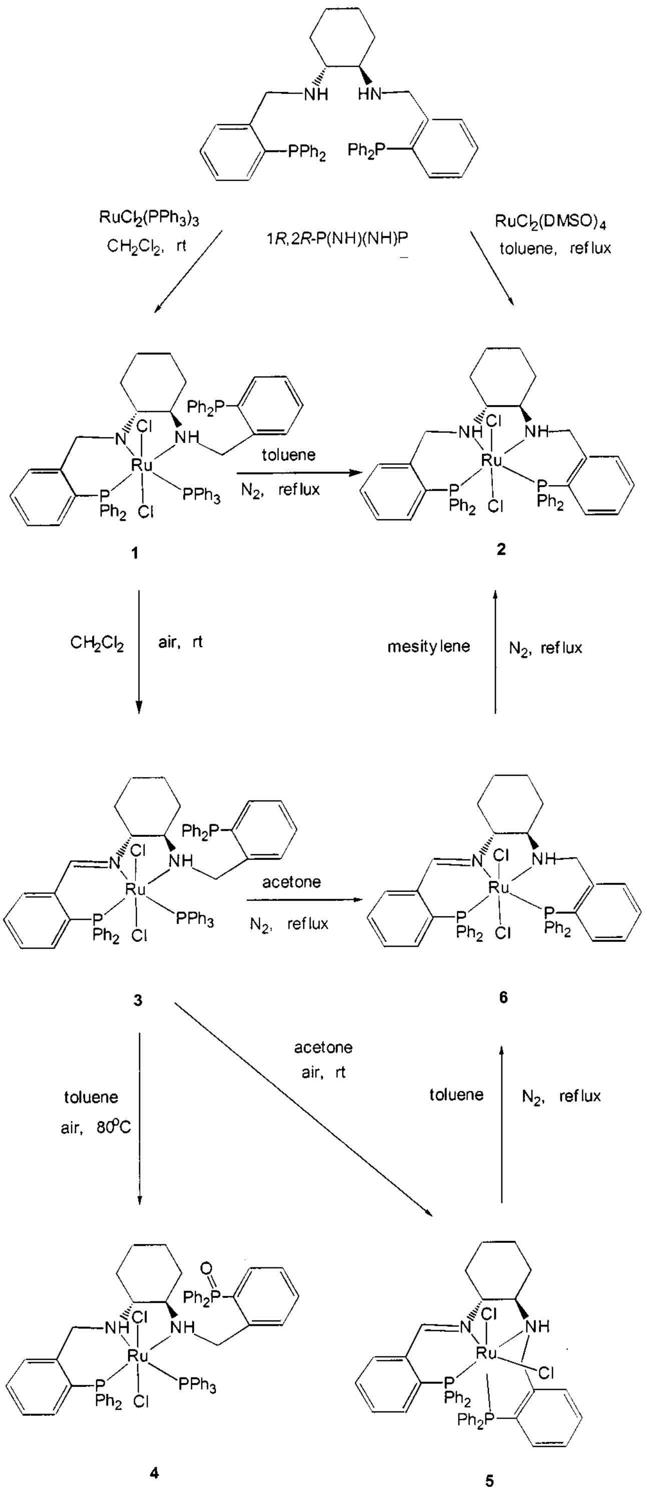
When heated to reflux in toluene under a nitrogen atmosphere, **1** was converted quantitatively to *trans*-[$RuCl_2\{\kappa^4$-1*R*,2*R*-P(NH)(NH)P}] (**2**), which was confirmed by comparing the spectroscopic data with the literature values.[1,7] However, when stirred in dichloromethane in air at room temperature, **1** was converted into *trans*-[$RuCl_2\{\kappa^3$-1*R*,2*R*-PN(NH)P}(PPh_3)] (**3**) (Scheme 1). The structure of **3** was established by X-ray crystallography (Figure 1). Selected bond lengths and bond angles are given in Table 1.

Structural analysis revealed that the κ^3-1*R*,2*R*-P(NH)(NH)P ligand had been oxidized to a κ^3-1*R*,2*R*-

---

[a] Department of Chemistry, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong, P. R. China
[b] Department of Chemistry, Tsinghua University, Beijing, 100084, P. R. China

1434−1948/02/0101−0231 $ 17.50+.50/0



Scheme 1

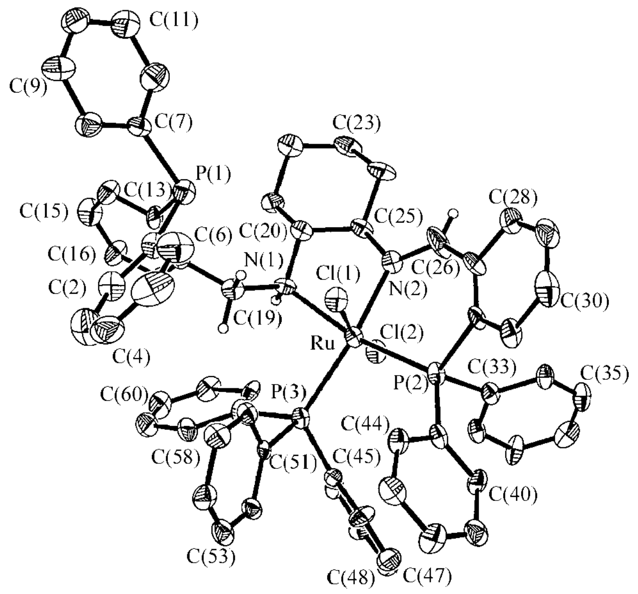


Figure 1. A perspective drawing of compound **3**. All the phenyl and cyclohexyl protons are omitted for clarity

Table 1. Selected bond lengths (Å) and bond angles (°) for compounds **3** and **5**

Compound **3**			
Ru−P(2)	2.261(2)	Ru−P(3)	2.355(2)
Ru−Cl(1)	2.452(2)	Ru−Cl(2)	2.405(2)
Ru−N(1)	2.192(6)	Ru−N(2)	2.059(7)
N(1)−C(19)	1.505(8)	N(1)−C(20)	1.488(8)
N(2)−C(25)	1.527(9)	N(2)−C(26)	1.28(1)
N(1)−Ru−N(2)	79.4(3)	N(1)−Ru−P(2)	168.2(2)
N(1)−Ru−P(3)	92.4(2)	N(1)−Ru−Cl(1)	86.4(2)
N(1)−Ru−Cl(2)	90.0(2)	N(2)−Ru−P(2)	89.6(2)
N(2)−Ru−P(3)	170.0(2)	N(2)−Ru−Cl(1)	81.7(2)
N(2)−Ru−Cl(2)	86.4(2)	P(2)−Ru−P(3)	98.9(1)
P(2)−Ru−Cl(1)	87.8(1)	P(2)−Ru−Cl(2)	93.6(1)
P(3)−Ru−Cl(1)	103.7(1)	P(3)−Ru−Cl(2)	87.9(1)
Cl(1)−Ru−Cl(2)	168.0(1)	N(1)−C(19)−C(18)	118.2(7)
N(2)−C(26)−C(27)	123(1)		

Compound **5**			
Ru−P(1)	2.299(2)	Ru−P(2)	2.270(2)
Ru−Cl(1)	2.453(1)	Ru−Cl(2)	2.442(1)
Ru−N(1)	2.026(5)	Ru−N(2)	2.142(4)
N(1)−C(1)	1.295(6)	N(1)−C(2)	1.521(7)
N(2)−C(8)	1.497(5)	N(2)−C(7)	1.500(6)
N(1)−Ru−N(2)	82.5(2)	N(1)−Ru−P(1)	94.9(1)
N(1)−Ru−P(2)	94.1(1)	N(1)−Ru−Cl(1)	85.1(1)
N(1)−Ru−Cl(2)	168.8(1)	N(2)−Ru−P(1)	90.3(1)
N(2)−Ru−P(2)	169.3(1)	N(2)−Ru−Cl(1)	80.8(1)
N(2)−Ru−Cl(2)	88.3(1)	P(1)−Ru−P(2)	100.2(1)
P(1)−Ru−Cl(1)	171.0(1)	P(1)−Ru−Cl(2)	91.5(1)
P(2)−Ru−Cl(1)	88.8(1)	P(2)−Ru−Cl(2)	93.8(1)
Cl(1)−Ru−Cl(2)	87.2(1)	N(1)−C(1)−C(27)	127.4(6)
N(2)−C(8)−C(9)	114.0(4)		

PN(NH)P ligand with the amino group *trans* to the PPh_3 group oxidized to an imino group. The N(1)−C(19) and N(2)−C(26) distances of 1.505(8) and 1.28(1) Å are consistent with a carbon−nitrogen single and double bond, respectively. The Ru atom adopts a slightly distorted octahedral geometry with a *trans*-$RuCl_2$ arrangement. The [1*R*,2*R*-PN(NH)P] ligand acts as a tridentate ligand with one of the two phosphanyl groups being uncoordinated. The sixth site is occupied by a PPh_3 ligand. The Ru−P, Ru−Cl, and Ru−N distances are in the range expected for similar complexes of general formula [RuCl$_2${P(NH)(NH)P}].[1,7,11] The Ru−N distances [Ru−N(1) 2.192(6), Ru−N(2) 2.059(7) Å] reflect that the imino nitrogen, N(2), is more tightly bound to the Ru centre than the amino nitrogen, N(1). The Ru−P distance of the PPh$_2$ group [Ru−P(2) 2.261(2) Å] is shorter than that of the PPh$_3$ group [Ru−P(3) 2.355(2) Å]. This may be a reflection of the chelate effect as well as the *trans* influence. The closing of the Cl(1)−Ru−Cl(2) angle [168.0°(1)] reflects the steric crowding and chelate ring strain in the complex, as the chloro ligands are pushed away from the bulky PPh$_3$ toward the imino moiety *trans* to it. The solid-state structure is supported by ^{1}H, ^{13}C and ^{31}P NMR, IR, and MS data. The ^{31}P{^{1}H} NMR spectrum of **3** exhibits two doublets and a singlet at δ = 55.5 (d, $^2J_{PP}$ = 27.2 Hz), 31.1 (d, $^2J_{PP}$ = 27.2 Hz), and −14.9 (s), which can be assigned to P(2), P(3), and P(1) (see Figure 1 for atom numbering), respectively. The presence of the imino group is further supported by the ^{1}H NMR spectrum and ^{13}C NMR spectrum, which shows a doublet at δ = 8.55 (d, $^4J_{P-CH}$ = 8.8 Hz, 1 H) for the proton and a singlet at δ = 164.9 for the carbon of the -CH=N- group. Furthermore, the IR spectrum shows the $\nu_{C=N}$ absorption at 1621 cm^{-1}. The positive FAB mass spectrum exhibits the molecular ion peak [M]$^+$ at *m/z* = 1094.

When heated to 80 °C in air in toluene, **3** was converted quantitatively to a purple red species, **4**, within 4 h. The ^{31}P{^{1}H} NMR spectrum of **4** exhibited two doublets and a singlet at δ = 47.1 (d, $^2J_{PP}$ = 28.8 Hz), 39.1 (d, $^2J_{PP}$ = 28.8 Hz), and 30.6 (s). The chemical shifts of the two doublets are very similar to those of **1**. Thus, the doublets at δ = 47.1 and 39.1 can be assigned to the phosphorus atoms of the tridentate ligand and PPh$_3$, respectively. The ^{31}P{^{1}H} NMR spectroscopic data suggest that the imino group in **3** has been reduced to an amino group. This is supported by the absence of the imino proton, imino carbon, and the $\nu_{C=N}$ band in the ^{1}H NMR, ^{13}C NMR, and IR spectra, respectively. The chemical shift of the singlet corresponds to that of a phosphane oxide, suggesting that the pendant phosphane had been oxidised to a phosphane oxide. This is further supported by the IR data, which shows the $\nu_{P=O}$ absorption at 1191 cm^{-1}, and the mass spectroscopic data (FAB, positive), which displays the molecular ion peak [M]$^+$ at *m/z* = 1112. Based on the spectroscopic data, compound **4** was formulated as *trans*-[RuCl$_2${κ^3-1*R*,2*R*-P(NH)(NH)P=O}(PPh$_3$)] with the structure shown in Scheme 1.

When stirred at room temperature in acetone in air, however, **3** was converted into a mixture of compounds. The ^{31}P NMR spectrum of the reaction mixture showed that in addition to **4** (approximately 5%), a new species **5** was also observed, which exhibited a pair of doublets at δ = 51.5 (d, $^2J_{PP}$ = 30.3 Hz) and 46.3 (d, $^2J_{PP}$ = 30.3 Hz). Compounds **4** and **5** could be easily separated by column chromatography. The structure of **5** was ascertained by X-ray crystallography (Figure 2). Crystals of **5**·H$_2$O suitable for X-ray diffraction study were grown by slow evaporation of **5** in an acetone/hexane mixture. The water molecule probably came from acetone, which had not been dried prior to use. Selected bond lengths and bond angles are given in Table 1. Structural analysis revealed that the tridentate κ^3-1*R*,2*R*-PN(NH)P ligand had become a tetradentate κ^4-1*R*,2*R*-PN(NH)P ligand with the imino nitrogen N(1) and the phosphorus atom P(1) of the aminophosphanyl group *trans* to the Cl atoms. The Ru atom had adopted a slightly distorted octahedral geometry with a *cis*-RuCl$_2$ arrangement. The Cl(1)−Ru−Cl(2) bond angle is 87.2(1)°. The Ru−P, Ru−Cl, and Ru−N distances are similar to those of **3**. The differences in Ru−P [Ru−P(1) 2.299(2), Ru−P(2) 2.270(2) Å], Ru−Cl [Ru−Cl(1) 2.453(1), Ru−Cl(2) 2.442(1) Å], and Ru−N [Ru−N(1) 2.026(5), Ru−N(2) 2.142(4) Å] distances are a reflection of the *trans* influence. The N(2)−C(8) and N(1)−C(1) distances of 1.497(5) and 1.295(6) Å are consistent with a carbon−nitrogen single and double bond, respectively.

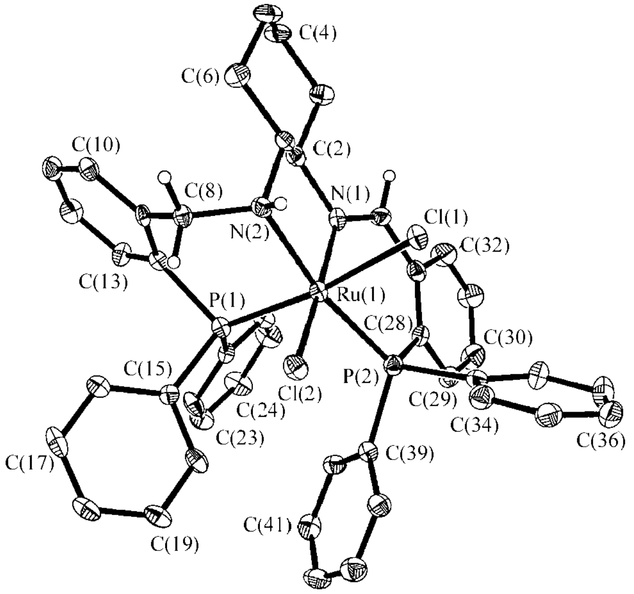


Figure 2. A perspective drawing of compound **5**; all the phenyl and cyclohexyl protons are omitted for clarity

When heated under reflux in toluene under a nitrogen atmosphere for 12 h, **5** was converted quantitatively (by ^{31}P NMR) to a red species **6**. In its ^{31}P NMR spectrum, **6** exhibited two doublets at δ = 54.3 (d, $^2J_{PP}$ = 26.7 Hz) and 36.1 (d, $^2J_{PP}$ = 26.7 Hz), which could be assigned to the PPh$_2$ groups attached to the imino and amino group, respectively. In its mass spectrum (FAB, positive), **6** exhibited the [M]$^+$ peak at *m/z* = 832 for ^{102}Ru and ^{35}Cl. Thus, compound **6** can be formulated as *trans*-[RuCl$_2${κ^4-1*R*,2*R*-PN(NH)P}]. Compound **6** could also be obtained quantitatively (by ^{31}P NMR) when an acetone solution of **3** was heated to reflux under a nitrogen atmosphere for 12 h. A ^{31}P NMR study showed that the imino group of **6** could be slowly reduced to an amino group upon prolong heating in a high boiling hydrocarbon solvent under a nitrogen atmosphere. When **6** was heated under reflux in mesitylene under a nitrogen atmosphere, the ^{31}P{^{1}H} NMR spectrum of the solution showed that as well as the resonances of **6**, a singlet at δ = 46.5 corresponding to a resonance of **2** emerged. After heating for 48 h under reflux the reaction proceeded cleanly with about 50% of **6** being converted into **2**, based on ^{31}P NMR spectroscopic data. No other phosphorus-containing species could be observed. The mechanism of this reduction is not clear, but it is very likely that the hydrogen source for the reduction is the solvent.

Catalytic Oxidation

Preliminary results showed that under oxygen, **1** catalysed the oxidation of octane primarily to 2-, 3-, and 4-octanone, hexene to 1,2-hexanediol, and styrene to benzoic acid (Table 2). For the octane oxidation, the effect of temperature was more critical than pressure. For example, when the catalytic reaction was carried out at 130 °C and an oxygen pressure of 5 MPa, the turnover frequency (TOF) was 67. A drop in oxygen pressure to 2.4 MPa did not affect the TOF significantly. The TOF was about 62. However, when the temperature was decreased to 110 °C, the TOF dropped to about 0.4. The activity of [$RuCl_2(PPh_3)_3$] as a catalyst for the oxidation of styrene and octane with oxygen were also examined. The results (the last two entries of Table 2) showed that under the same conditions [$RuCl_2(PPh_3)_3$] catalysed the oxidation of styrene with oxygen to benzaldehyde and styrene oxide with a very low conversion (0.4%), and was inactive toward the oxidation of octane with oxygen. Thus, **1** is a better catalyst than [$RuCl_2(PPh_3)_3$] for the oxidation of styrene and octane with oxygen.

Ruthenium-catalysed oxidation of alkane with peroxo species has drawn considerable interest recently. However, most of the studies were concentrated on the use of peroxo species as oxidants in the catalytic reaction;[12−14] there were very few studies using molecular oxygen as oxidant.[15] The present study provides an additional example of a catalytic system where molecular oxygen can be used to oxidise a saturated hydrocarbon. The mechanism of the catalytic oxidation is not clear. However, based on the reactivity of **1** with air, compounds **3** and **4** may be involved as intermediates in the catalytic cycle. The transformation of **3** to **4** is rather unusual. Rather than just oxidising the pendant phosphane to a phosphane oxide, the oxidation was accompanied by the reduction of an imino group to an amino group.

Experimental Section

General Procedures: Unless otherwise stated, all reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk and vacuum-line techniques. Solvents were dried by standard procedures, distilled, and deaerated prior to use. All chemicals

Table 2. Catalytic oxidation of 1-hexene, styrene and octane with O_2 using **1** as catalyst

Substrate	Temp (°C)	O_2 Pressure (MPa)	Conversion (%)[a]	TOF (h^{-1})[a]	Product[b]	Selectivity (%)[c]
1-Hexene[d]	130	5.0	39	4633	1,2-hexanediol	55
Styrene[e]	130	3.9	93	3038	benzaldehyde	1
					benzoic acid	85
Octane[f]	130	5.0	70	67	butanoic acid	12
					4-octanone	11
					3-octanone	12
					2-octanone	25
					4-octanol	0.2
					3-octanol	0.2
					2-octanol	0.4
	130	2.4	57	62	butanoic acid	9
					4-octanone	12
					3-octanone	16
					2-octanone	23
					4-octanol	0.7
					3-octanol	1
					2-octanol	1.3
	110	4.4	0.4	0.4	butanoic acid	10
					4-octanone	43
					3-octanone	25
					2-octanone	22
Styrene[g]	130	3.9	0.4	11	benzaldehyde	75
					styrene oxide	21
Octane[h]	130	2.4	0	0	−	0

[a] Determined by GLC analysis based on the starting substrate using acetophenone as an internal standard. [b] Identified by GC-MS. [c] Determined by GLC analysis based on the converted substrate using acetophenone as an internal standard. [d] Substrate (2.0 g): catalyst (1 mg) = 26100 (mole ratio), reaction time = 2 h. [e] Substrate (2.7 g): catalyst (2 mg) = 14200 (mole ratio), reaction time = 4 h. [f] Substrate (1.4 g): catalyst (2 mg) = 6700 (mole ratio), reaction time = 64 h. [g] Catalyst: $RuCl_2(PPh_3)_3$, substrate (2.7 g): catalyst (2 mg) = 12500 (mole ratio), reaction time = 4 h. [h] Catalyst: $RuCl_2(PPh_3)_3$, substrate (1.4 g): catalyst (2 mg) = 5900 (mole ratio), reaction time = 17 h.

used were of reagent grade, obtained from the Aldrich Chemical Company, and, where appropriate, were degassed before use. The compounds 1*R*,2*R*-P(NH)(NH)P[8] and [RuCl$_2$(PPh$_3$)$_3$][16] were prepared according to literature methods. Microanalyses were performed at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The IR spectra (KBr pellets) were recorded on a Nicolet Nagna-IR 550 spectrometer, and NMR spectra on a JEOL EX270 spectrometer. Chemical shifts of ^{1}H NMR spectra were referenced to internal deuterated solvents and then recalculated to TMS (δ = 0.00), those of ^{31}P{^{1}H} NMR spectra were referenced to external 85% H_3PO_4. Low-resolution mass spectra were obtained on a Finnigan MAT SSQ-710 or MAT 95 spectrometer in positive FAB mode and reported as *m*/*z*. Gas chromatograms were obtained on a HP 5890 GC system or a HP 6890−5972 GC-MSD system. The progress of all the reactions was monitored by ^{31}P{^{1}H} NMR spectroscopy.

Preparation of *trans*-[RuCl$_2${κ^3-1*R*,2*R*-P(NH)(NH)P}(PPh$_3$)] (1): A solution of 1*R*,2*R*-P(NH)(NH)P (0.212 g, 0.320 mmol) and [RuCl$_2$(PPh$_3$)$_3$] (0.305 g, 0.318 mmol) in CH_2Cl_2 (20 cm^3) was stirred under a nitrogen atmosphere at room temperature for 4 h. The solution was filtered and the solvent of the filtrate was removed in vacuo to give a dark red residue. The residue was dissolved in a minimum amount of chloroform and purified by chromatography on a silica gel column using chloroform as eluent to give an orange band. Removal of the solvent from the orange band gave an orange solid, which was recrystallized from dichloromethane/hexane to give orange crystals. Yield: 0.264 g, 64%; m.p. 186−187 °C (decomp). IR (KBr): ṽ = 3257 cm^{-1} w, 3186 w, 3047 m, 2930 w, 1490 m, 1434 s, 1189 w, 1086 m, 1035 w, 994 m, 958 w, 753 s, 702 vs, 574 w, 552 s and 467 w. ^{1}H NMR: (CDCl$_3$): δ = 6.41−7.82 (m, 43 H), 3.98 (m, 2 H), 3.79 (m, 2 H), 3.53 (m, 2 H), 3.04 (m, 1 H), 2.57 (m, 1 H), 0.98−1.48 (m, 8 H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 47.0 (d, $^2J_{PP}$ = 28.2 Hz), 39.3 (d, $^2J_{PP}$ = 28.2 Hz), −13.1 (s). $C_{62}H_{59}Cl_2N_2P_3Ru{\cdot}CH_2Cl_2{\cdot}CHCl_3$ (1301.37): calcd. C 59.07, H 4.80, N 2.15; found C 59.09, H 4.81 , N 2.14. LRMS (FAB+): *m*/*z* = 1096 [M]$^+$ for ^{102}Ru and ^{35}Cl. $[\alpha]^{20}_{D}$ = 55.83 (*c* = 0.5, CH_2Cl_2).

Preparation of *trans*-[RuCl$_2${κ^4-1*R*,2*R*-P(NH)(NH)P}] (2): A solution of **1** (0.081 g, 0.074 mmol) in toluene (10 cm^3) was heated to reflux under a nitrogen atmosphere for 12 h. After cooling to room temperature, the solution was filtered, and the solvents evaporated to dryness in vacuo to give an orange residue. The residue was washed with diethyl ether (2 × 5 cm^3) and recrystallized from a CH_2Cl_2/hexane mixture to give orange crystals of **2**. Yield: 0.060 g, 97% (0.072 mmol). The identity of **2** was confirmed by comparing the IR, NMR [^{1}H and ^{31}P{^{1}H}], and MS (FAB+) data of **2** with those of an authentic sample of *trans*-[RuCl$_2${κ^4-1*R*,2*R*-P(NH)(NH)P}].

Preparation of *trans*-[RuCl$_2${κ^3-1*R*,2*R*-PN(NH)P}(PPh$_3$)] (3): A solution of **1** (0.020 g, 0.018 mmol) in dichloromethane (5 cm^3) was allowed to stir at room temperature in air. The progress of the reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy. After 2 days, the ^{31}P NMR spectrum showed that **1** had completely reacted. The solution was then filtered and the filtrate was evaporated to dryness. The residue was dissolved in a minimum amount of chloroform and purified by chromatography on a silica gel column using chloroform as eluent to give a red band, which upon workup and crystallisation from a CHCl$_3$/THF/hexane mixture gave red crystals of **3**. Yield: 0.018 g, 91%; m.p. 148−149 °C (decomp). IR (cm^{-1}, in KBr): ṽ = 3258 w, 3058 m, 2929 m, 2865 w, 1621 m, 1584 w, 1481 m, 1430 s, 1093 m, 751 s, 705 vs and 524 s. ^{1}H NMR (CDCl$_3$): δ = 8.55 (d, $^4J_{P-H}$ = 8.8 Hz, 1 H), 5.94−8.02 (m, 43 H), 4.55 (m, 1 H), 3.86−4.21 (m, 4 H), 3.03 (m, 1 H), 2.26 (m, 1 H), 0.96−1.35 (m, 6 H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 164.9 (s), 126.8−136.1 (m), 64.5 (s), 53.7 (s), 43.6 (s), 40.4 (s), 29.2(s). ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 55.5 (d, $^2J_{PP}$ = 27.2 Hz), 31.1 (d, $^2J_{PP}$ = 27.2 Hz), −14.9 (s). $C_{62}H_{57}Cl_2N_2P_3Ru{\cdot}CH_2Cl_2{\cdot}C_6H_{14}$ (1266.15): calcd. C 65.46, H 5.81, N 2.21; found C 65.09, H 5.86, N 2.19. LRMS (FAB+): *m*/*z* = 1094 [M]$^+$ for ^{102}Ru and ^{35}Cl. $[\alpha]^{20}_{D}$ = 60.90 (*c* = 0.5, CH_2Cl_2).

Preparation of *trans*-[RuCl$_2${κ^3-1*R*,2*R*-P(NH)(NH)P=O}(PPh$_3$)] (4): A solution of **3** (0.050 g, 0.046 mmol) in toluene (10 cm^3) was heated to 80 °C in air. After heating at 80 °C in air for 4 h, the solution turned purple red and the ^{31}P NMR signals due to **3** had completely disappeared. The solvent was subsequently removed in vacuo to give a purple red residue, which upon crystallization from a CHCl$_3$/THF/hexane mixture gave purple red crystals. Yield: (quantitative by ^{31}P{^{1}H} NMR), 0.050 g, 98%; m.p. 198−199 °C (decomp). IR (KBr): ṽ = 3263 cm^{-1} w, 3048 m, 2929 w, 2852 w, 1584 w, 1486 m, 1429 s, 1305 w, 1264 m, 1191 s, 1124 s, 1088 s, 1026 m, 995 m, 803 m, 747 s, 721 s, 695 vs, 550 vs and 534 s. ^{1}H NMR (CDCl$_3$): δ = 6.20−8.10 (m, 43 H), 3.91 (m, 4 H), 3.57 (m, 2 H), 3.05 (m, 1 H), 2.65 (m, 1 H), 0.80−1.60 (m, 8 H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 126.8−136.6 (m), 60.8 (s), 49.0 (s), 48.7 (s), 31.1 (s), 24.8 (s). ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 47.1 (d, $^2J_{PP}$ = 28.8 Hz), 39.1 (d, $^2J_{PP}$ = 28.8 Hz), 30.6 (s). $C_{62}H_{59}Cl_2N_2OP_3Ru{\cdot}C_4H_{10}O{\cdot}CHCl_3$ (1304.54): calcd. C 61.69, H 5.25, N 2.15; found C 61.51, H 5.75, N 2.01. LRMS (FAB+): *m*/*z* = 1112 [M]$^+$ for ^{102}Ru and ^{35}Cl. $[\alpha]^{20}_{D}$ = 34.95 (*c* = 0.5, CH_2Cl_2).

Preparation of *cis*-[RuCl$_2${κ^4-1*R*,2*R*-PN(NH)P}] (5): A solution of **3** (0.050 g, 0.046 mmol) in acetone (10 cm^3) was stirred in air at room temperature for 4 days. The solution was filtered and the solvent from the filtrate was removed in vacuo to give a dark red residue. The residue was dissolved in a minimum amount of chloroform and purified by chromatography on a silica gel column using chloroform as eluent to give a red band. This was followed by eluting with acetone to afford another red band. The red band from chloroform, after work up, was identified as the starting material **3** (0.028 g, 56% recovery).

Removal of the solvent from the second red band led to a red solid, which upon crystallisation from a CHCl$_3$/THF/hexane mixture gave red crystals of **5**. Yield: 0.016 g, 42%; m.p. 102−104 °C (decomp). IR (KBr): ṽ = 3253 cm^{-1} w, 3058 m, 2924 m, 1623 m, 1486 m, 1439 s, 1113 m, 761 s, 710 vs and 539 s. ^{1}H NMR (CDCl$_3$): δ = 8.69 (s, 1 H), 6.00−7.89 (m, 28 H), 4.85 (m, 1 H), 4.10−4.28 (m, 2 H), 3.61 (m, 1 H), 2.99 (m, 1 H), 1.93−2.38 (m, 3 H), 0.88−1.40 (m, 5 H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 51.5 (d, $^2J_{PP}$ = 30.3 Hz), 46.3 (d, $^2J_{PP}$ = 30.3 Hz). $C_{44}H_{42}Cl_2N_2P_2Ru{\cdot}3H_2O$ (886.80): calcd. C 59.59, H 5.46, N 3.16; found C 59.05, H 5.75, N 3.25. LRMS (FAB+): *m*/*z* = 832 [M]$^+$ for ^{102}Ru and ^{35}Cl. $[\alpha]^{20}_{D}$ = 60.18 (*c* = 0.5, CH_2Cl_2).

Preparation of *trans*-[RuCl$_2${κ^4-1*R*,2*R*-PN(NH)P}] (6). Method (a): A solution of **5** (0.030 g, 0.036 mmol) in toluene (10 cm^3) was heated under reflux overnight under a nitrogen atmosphere. The solution was filtered and the solvent from the filtrate was removed in vacuo to give a dark red residue. The dark residue was washed with Et_2O (2 × 5 cm^3) and recrystallized from a dichloromethane/hexane mixture to give red crystals of **6**. Yield: 0.029 g, 97%; m.p. 198−200 °C. IR (KBr): ṽ = 3258 cm^{-1} w, 3054 m, 2924 m, 1629 m, 1481 m, 1430 s, 1114 m, 747 s, 700 vs and 524 s. ^{1}H NMR (CDCl$_3$): δ = 9.41 (s, 1 H), 6.21−7.83 (m, 28 H), 4.55 (m, 2 H), 3.68 (m, 1 H), 2.21−2.80 (m, 4 H), 1.01−1.56 (m, 6 H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 54.3 (d, J_{PP} = 26.7 Hz), 36.1 (d, J_{PP} =

Table 3. Crystallographic data for compounds **3** and **5**

Compound	**3**	**5**
Empirical formula	$C_{62}H_{57}Cl_2N_2P_3Ru \cdot C_4H_8O$	$C_{44}H_{42}Cl_2N_2P_2Ru \cdot H_2O$
Formula mass	1167.08	850.71
Colour and habit	Red block	Red block
Crystal size/mm	0.10 × 0.10 × 0.15	0.10 × 0.12 × 0.15
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	10.349(1)	12.705(1)
b/Å	17.752(2)	13.393(1)
c/Å	31.719(3)	22.432(2)
V/Å^3	5827(1)	3817.0(6)
Z	4	4
$D_{\text{calcd.}}$/g·cm^{-3}	1.330	1.477
Absorption coefficient/mm^{-1}	0.487	0.673
F(000)	2424	1744
Θ range/°	1.72 to 27.53	1.77 to 27.54
Reflections collected	34944	22625
Independent reflections	13174 (R_{int} = 0.1841)	8598 (R_{int} = 0.0957)
Goodness-of-fit on F^2	0.712	0.744
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0546 $wR2$ = 0.0853	$R1$ = 0.0458 $wR2$ = 0.0607

26.7 Hz). $C_{44}H_{42}Cl_2N_2P_2Ru \cdot CH_2Cl_2 \cdot C_6H_{14}$ (1003.86): calcd. C 61.02, H 5.82, N 2.79; found C 60.33, H 5.31, N 2.36. LRMS (FAB+): m/z = 832 [M]$^+$ for ^{102}Ru and ^{35}Cl. $[\alpha]_D^{20}$ = 56.07 (c = 0.5, CH_2Cl_2).

Method (b): A solution of **3** (0.050 g, 0.046 mmol) in acetone (10 cm^3) was heated to reflux under a nitrogen atmosphere for 12 h. The solution was filtered and the solvent was removed in vacuo from the filtrate to give a dark red residue. The dark residue was washed with Et_2O (2 × 5 cm^3) and recrystallized from a chloroform/hexane mixture to give red crystals of **6**. Yield: 0.037 g, 97%.

Thermolysis of 6: A solution of **6** (0.020 g, 0.024 mmol) in mesitylene (10 cm^3) was heated under reflux under a nitrogen atmosphere for 48 h. The ^{31}P{^{1}H} NMR spectrum of the solution showed that as well as the resonances due to **6**, a new singlet at δ = 46.5 had appeared. The solution was filtered and the solvent removed from the filtrate in vacuo, to give a dark red residue. The residue was dissolved in a minimum amount of chloroform and purified by chromatography on a silica gel column using chloroform as eluent to give two red bands. Work up of the first band gave orange crystals of **2** (0.010 g, 50% yield) and second band red crystals of **6** (0.009 g, 45% recovery). Their identities were confirmed by comparing their IR, NMR (^{1}H and ^{31}P), and MS (FAB+) data with those of authentic samples of **2** and **6**.

Catalytic Studies: Catalytic experiments were carried out in a 50-cm^3 stainless steel autoclave (model FW-005) equipped with a temperature control unit. ***Caution:*** *The catalytic reactions must be carried out with safety protection as the reactions may become very violent and explode.* All the catalytic reactions, unless otherwise stated, were carried out in the absence of any solvent. Upon transferring the catalyst, the substrate and a magnetic stirring bar to the autoclave, the autoclave was flushed with oxygen three times by pressurising the autoclave to the desired pressure for 30 s before releasing the pressure. After the autoclave had been thoroughly flushed with oxygen, it was pressurised to the desired oxygen pressure, stirred and quickly raised to the desired temperature. The reaction mixture was allowed to react at the desired temperature for the desired period before it was cooled to room temperature. Then the pressure of the autoclave was released slowly and the reaction mixture was analysed by GC. The identities of the products were verified by GC-MS. Control experiments without the catalysts were performed under identical conditions. The results of the catalytic studies are listed in Table 2.

X-ray Crystallography: Pertinent crystallographic data and other experimental details are summarized in Table 3. Crystals of **3**·C_4H_8O and **5**·H_2O suitable for X-ray diffraction study were grown by slow evaporation of **3** in a THF/hexane mixture and **5** in an acetone/hexane mixture, respectively. The crystals were wrapped in epoxy glue to prevent them from losing solvent, and mounted on a thin glass fibre. No decay in intensity was encountered during the data collection. Intensity data were collected at 293 K on a Bruker Axs SMART 1000 CCD area-detector diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The collected frames were processed with the software SAINT[17] and an absorption correction was applied (SADABS)[18] to the collected reflections. The space groups of each crystal were determined from the systematic absences and Laue symmetry check and confirmed by successful refinement of the structure. The structures of all compounds were solved by direct methods (SHELXTL)[19] and refined against F^2 by full-matrix least-squares analysis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated in their idealized positions and allowed to ride on their respective parent carbon atoms. The Flack parameter for compounds **3** and **5** is 0.07(4) and −0.04(3), respectively.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-161383 (**3**) and CCDC-164794 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

W.-K. Wong thanks the Hong Kong Baptist University and the Hong Kong Research Grants Council (HKBU 2053/97P) for financial support.

---

[1] J. X. Gao, T. Ikariya, R. Noyori, *Organometallics* **1996**, *15*, 1087−1089.

[2] R. M. Stoop, A. Mezzetti, *Green Chemistry* **1999**, 39−41.

[3] B. M. Trost, *Acc. Chem. Res.* **1996**, *29*, 355−364.

[4] C. P. Butts, J. Crosby, G. C. Lloyd-Jones, S. C. Stephen, *Chem. Commun.* **1999**, 1707−1708 and refs. therein.

[5] W. K. Wong, J. X. Gao, Z. Y. Zhou, T. C. W. Mak, *Polyhedron* **1993**, *12*, 1415−1417.

[6] J. X. Gao, H. L. Wan, W. K. Wong, M. C. Tse, W. T. Wong, *Polyhedron* **1996**, *15*, 1241−1251.

[7] W. K. Wong, T. W. Chik, X. Feng, T. C. W. Mak, *Polyhedron* **1996**, *15*, 3905−3907.

[8] W. K. Wong, T. W. Chik, K. N. Hui, I. Williams, X. Feng, T. C. W. Mak, C. M. Che, *Polyhedron* **1996**, *15*, 4447−4460.

[9] W. K. Wong, J. X. Gao, W. T. Wong, C. M. Che, *Polyhedron* **1993**, *12*, 2063−2066.

[10] W. K. Wong, J. X. Gao, W. T. Wong, W. C. Cheng, C. M. Che, *J. Organomet. Chem.* **1994**, *471*, 277−282.

[11] R. M. Stoop, S. Bachmann, M. Valentini, A. Mezzetti, *Organometallics* **2000**, *19*, 4117−4126.

[12] C. M. Che, K. W. Cheng, M. C. W. Chan, T. C. Lau, C. K. Mak, *J. Org. Chem.* **2000**, *65*, 7996−8000.

[13] S. I. Murahashi, N. Komiya, Y. Oda, T. Kuwabara, T. Naota, *J. Org. Chem.* **2000**, *65*, 9186−9193.

[14] N. Komiya, S. Noji, S. I. Murahashi, *Chem. Commun.* **2001**, 65−66.

[15] A. S. Goldstein, R. H. Beer, R. S. Drago, *J. Am. Chem. Soc.* **1994**, *116*, 2424−2429.

[16] S. J. La Placa, J. A. Ibers, *Inorg. Chem.* **1965**, *4*, 778−783.

[17] *SAINT, Reference Manual*, Siemens Energy and Automation, Madison, WI, **1994−1996**.

[18] G. M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Göttingen, **1997**.

[19] G. M. Sheldrick, *SHELXTL Reference Manual, ver.5.1*, Siemens, Madison, WI, **1997**.

Received June 11, 2001
[I01212]