DALTON
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# Synthesis, structure and catalytic activity of ruthenium diaminodiphosphine complexes

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

[a] *Department of Chemistry, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong, P.R. China. E-mail: wkwong@hkbu.edu.hk*
[b] *Department of Chemistry, Tsinghua University, Beijing, 100084, P.R. China*

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The reaction of *N,N′*-bis[*o*-(diphenylphosphino)benzylidene]-1,2-diaminoethane ($L^2$) with one equivalent of $RuCl_2(PPh_3)_3$ in dichloromethane at room temperature gave *trans*-$RuCl_2(PPh_3)(\kappa^3\text{-}L^2)$ **2** in high yield. When refluxed in toluene in air, **2** was converted quantitatively to *trans*-$RuCl_2(\kappa^4\text{-}L^2)$ **3**. When treated with one equivalent of hydrogen peroxide in chloroform, **2** was oxidized to *trans*-$RuCl_2(PPh_3)(\kappa^3\text{-}L^3)$ **4**, in which the pendant phosphine has been oxidized to a phosphine oxide. Complex **4** can be further oxidized with another equivalent of hydrogen peroxide to *trans*-$RuCl_2(PPh_3)(\kappa^3\text{-}L^4)$ **5**, in which the amino group *trans* to $PPh_3$ has been oxidized to an imino group. When treated with excess hydrogen peroxide in ethanol, **3** was oxidized to *trans*-$RuCl_2(\kappa^4\text{-}L^5)$ **6**, in which the diamino moiety [–N(H)$CH_2CH_2$N(H)–] has been oxidized to a conjugated diimino moiety (–N=CHCH=N–). The solid-state structures of **2**, **4**, **5** and **6** were ascertained by X-ray crystallography. Catalytic studies show that **2** is an effective catalyst for the oxidation of alkanes, alkenes and alcohols with air or *tert*-butyl hydroperoxide. Experimental evidence suggests that free radicals are probably involved in the catalytic oxidation processes.

## Introduction

Diamino-, diimino- and diamidodiphosphine ligands are very versatile ligands. These ligands exhibit very rich coordination chemistry and, depending on the reaction conditions, can behave as bridging, bi-, tri- and tetradentate ligands.[1–8] Recently, there has been considerable interest in the preparation and chemistry of transition metal complexes with chiral diamino-, diimino- and diamidodiphosphine ligands[9–18] as they have been shown to be effective catalysts for asymmetric hydrogen transfer reactions,[12] epoxidation,[13,14] cyclopropanation[15] and allylic alkylation.[16–18] *N,N′*-bis[*o*-(diphenylphosphino)benzylidene]-1,2-diiminoethane ($L^1$, see Chart 1) and *N,N′*-bis[*o*-(diphenylphosphino)benzylidene]-1,2-diaminoethane ($L^2$) are amongst the very first non-chiral diimino- and diaminodiphosphines to be synthesized.[7] However, there have been relatively few studies on the chemistry and catalytic activities of their transition metal complexes as compared to their chiral analogues. We have reported the synthesis of *trans*-$RuCl_2(\kappa^4\text{-}L^1)$ and *trans*-$RuCl_2(\kappa^4\text{-}L^2)$, and shown that they are effective catalysts for the hydrogenation of acrylic acid to propionic acid.[5] Here, we describe the synthesis and reactivity of the novel complex *trans*-$RuCl_2(PPh_3)(\kappa^3\text{-}L^2)$, prepared *via* the reaction of $RuCl_2(PPh_3)_3$ with $L^2$. Catalytic studies show that *trans*-$RuCl_2(PPh_3)(\kappa^3\text{-}L^2)$ is an effective catalyst for the oxidation of alkanes, alkenes and alcohols with air or *tert*-butyl hydroperoxide.

## Results and discussion

### Synthesis and characterization of ruthenium complexes

At room temperature in dichloromethane, $RuCl_2(PPh_3)_3$ reacted with one equivalent of $L^1$ and $L^2$ to give *trans*-$RuCl_2(\kappa^4\text{-}L^1)$ **1**[5] and *trans*-$RuCl_2(PPh_3)(\kappa^3\text{-}L^2)$ **2**, respectively, in high yield (Scheme 1). The structure of **2**, which was ascertained by X-ray crystallography (Fig. 1), is similar to that of the recently reported *trans*-$RuCl_2(PPh_3)\{\kappa^3\text{-}(1R,2R)\text{-}L^6\}$ {$(1R,2R)$-$L^6$ = $(1R,2R)$-*N,N′*-bis[*o*-(diphenylphosphino)benzylidene]-1,2-di-

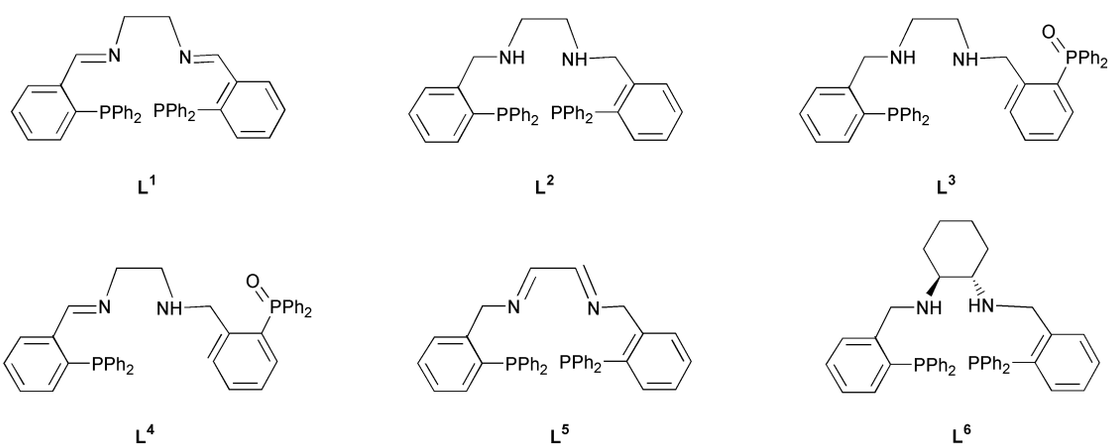
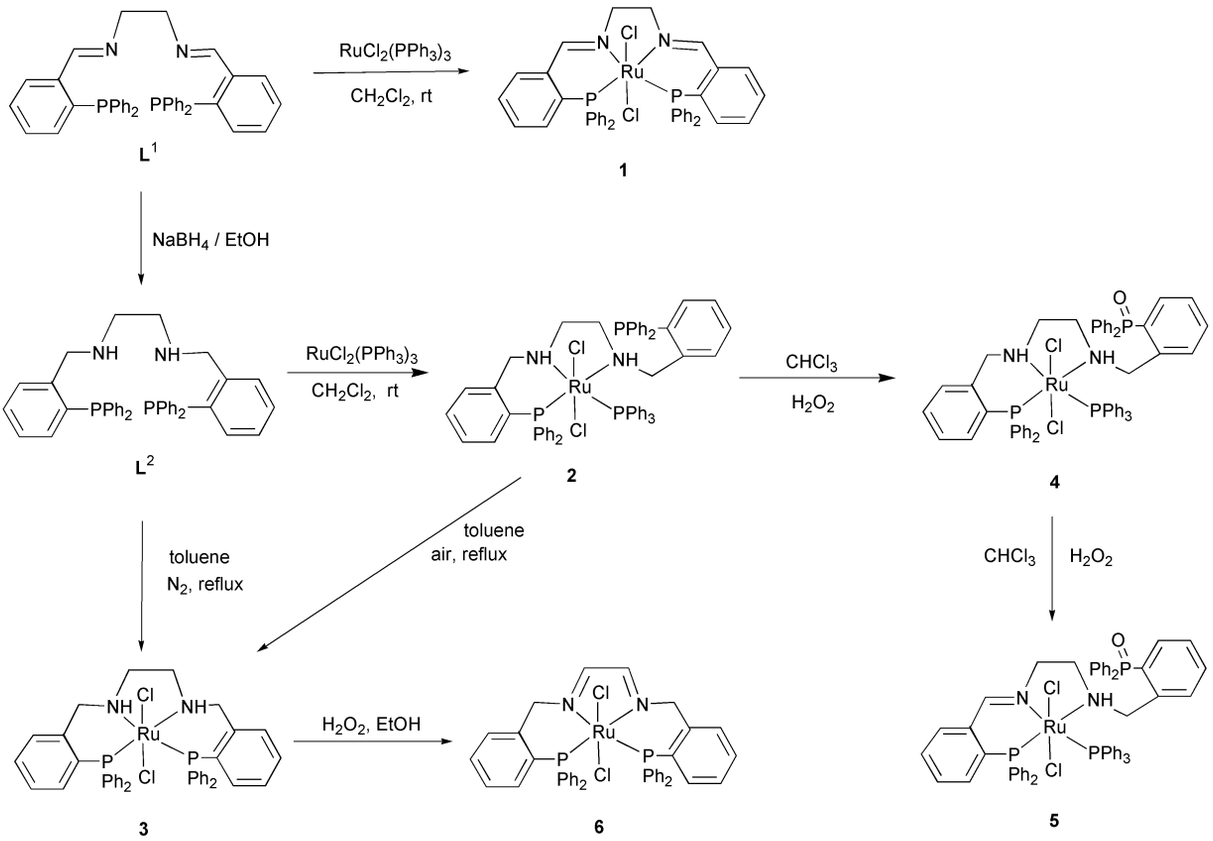



**Chart 1**




**Scheme 1**

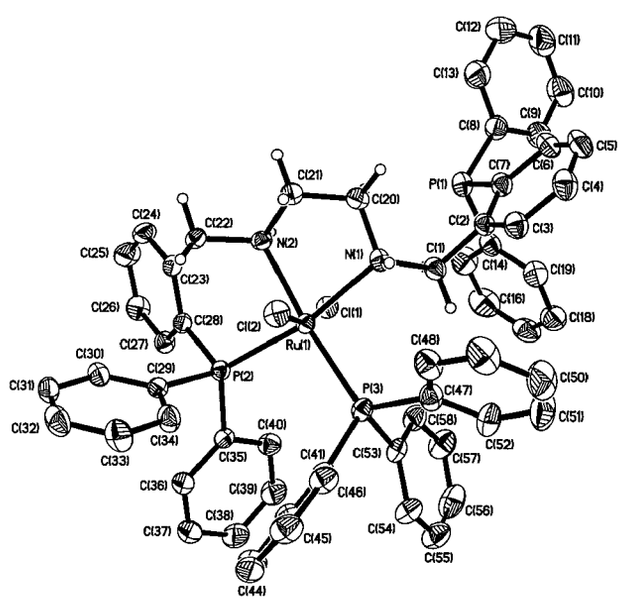


**Fig. 1** A perspective drawing of compound **2**, with the atoms shown at the 30% probability level. Hydrogen atoms of all phenyl rings are omitted for clarity.

aminocyclohexane}.[14,19] Selected bond lengths and bond angles of **2** are given in Table 1. Structural analysis revealed that the Ru atom adopts a slightly distorted octahedral geometry with a *trans*-$RuCl_2$ arrangement. The $L^2$ ligand acts as a tridentate ligand with a pendant $PPh_2$ group. The sixth site is occupied by a $PPh_3$ ligand, which is *cis* to the coordinated $PPh_2$ group of the $L^2$ ligand. The Ru–P, Ru–Cl and Ru–N distances are in the ranges expected for similar complexes of general formula $RuCl_2$[P(NH)(NH)P] [P(NH)(NH)P = $L^2$ and $L^6$].[10,12,14] The differences in the Ru–N [Ru(1)–N(1) 2.226(3), Ru(1)–N(2) 2.162(3) Å] and Ru–P [Ru(1)–P(2) 2.2987(9), Ru(1)–P(3) 2.346(1) Å] distances is a reflection of the chelate effect. The closing of the Cl(1)–Ru(1)–Cl(2) angle [165.9°(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 amino moiety *trans* to it. The spectroscopic data are consistent with the solid-state structure. The $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits two doublets and a singlet at $\delta$ 48.6 (d, $^2J_{PP}$ = 28.9 Hz), 38.9 (d, $^2J_{PP}$ = 28.9 Hz) and −13.3 (s) for P(2), P(3) and P(1), respectively, and its mass spectrum (positive FAB) shows a peak corresponding to its molecular ion $(M + 1)^+$ at *m*/*z* 1042.

When refluxed in toluene in air, **2** lost the $PPh_3$ ligand to give *trans*-$RuCl_2(\kappa^4\text{-}L^2)$ **3**, which could also be obtained by reacting $L^2$ with $RuCl_2(DMSO)_4$ in refluxing toluene.[5] When reacted with excess $H_2O_2$ at room temperature, **2** was oxidized to a complex mixture. However, the degree of oxidation could be controlled by the amount of $H_2O_2$ added. When treated with one equivalent of $H_2O_2$, **2** was slowly oxidized to *trans*-$RuCl_2(PPh_3)(\kappa^3\text{-}L^3)$ **4**. The progress of the oxidation was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The pendant phosphine at $\delta$ −13.3 (s) was slowly converted to the phosphine oxide at $\delta$ 29.2 (s). This is further supported by the mass spectral data (positive FAB), which exhibits the molecular ion peak $(M + 1)^+$ at *m*/*z* 1058, which is 16 mass units more than that of **2**. The structure of **4** was confirmed by X-ray crystallography (Fig. 2). Selected bond lengths and bond angles are given in Table 1. Structural analysis revealed that other than the pendant phosphine of the tridentate ligand $\kappa^3$-$L^2$ being oxidized to the phosphine oxide, the structure of **4** is very similar to that of **2**. The Ru atom adopts a slightly distorted octahedral geometry with a *trans*-$RuCl_2$ arrangement and a Cl(1)–Ru(1)–Cl(2) angle of 166.3(1)°. The $L^3$ ligand acts as a tridentate ligand with the $PPh_2$ group *cis* to $PPh_3$. The Ru–P, Ru–Cl and Ru–N distances are similar to those of **2**. The differences in the Ru–N [Ru(1)–N(1) 2.226(3), Ru(1)–N(2) 2.158(3) Å] and Ru–P [Ru(1)–P(2) 2.287(1), Ru(1)–P(3) 2.342(1) Å] distances is again a reflection of the chelate effect. The $^{31}P\{^1H\}$ NMR spectrum of **4** is

**Table 1** Selected bond lengths (Å) and bond angles (°) for compounds **2**, **4**, **5** and **6**

| Compound **2** | | Compound **4** | | Compound **5** | | Compound **6** | |
|---|---|---|---|---|---|---|---|
| Ru(1)–P(2) | 2.2987(9) | Ru(1)–P(2) | 2.287(1) | Ru(1)–P(2) | 2.273(1) | Ru(1)–P(1) | 2.345(1) |
| Ru(1)–P(3) | 2.346(1) | Ru(1)–P(3) | 2.342(1) | Ru(1)–P(3) | 2.357(1) | Ru(1)–P(2) | 2.332(1) |
| Ru(1)–N(1) | 2.226(3) | Ru(1)–N(1) | 2.226(3) | Ru(1)–N(1) | 2.228(2) | Ru(1)–N(1) | 2.050(2) |
| Ru(1)–N(2) | 2.162(3) | Ru(1)–N(2) | 2.158(3) | Ru(1)–N(2) | 2.073(3) | Ru(1)–N(2) | 2.048(2) |
| Ru(1)–Cl(1) | 2.4527(9) | Ru(1)–Cl(1) | 2.416(1) | Ru(1)–Cl(1) | 2.407(5) | Ru(1)–Cl(1) | 2.407(8) |
| Ru(1)–Cl(2) | 2.4191(9) | Ru(1)–Cl(2) | 2.402(1) | Ru(1)–Cl(2) | 2.438(9) | Ru(1)–Cl(2) | 2.415(8) |
| N(1)–C(1) | 1.497(4) | N(1)–C(19) | 1.490(4) | N(1)–C(19) | 1.483(4) | N(1)–C(19) | 1.452(4) |
| N(1)–C(20) | 1.501(5) | N(1)–C(20) | 1.498(4) | N(1)–C(20) | 1.487(4) | N(1)–C(20) | 1.294(4) |
| N(2)–C(21) | 1.483(5) | N(2)–C(21) | 1.455(4) | N(2)–C(21) | 1.463(4) | N(2)–C(21) | 1.284(4) |
| N(2)–C(22) | 1.489(4) | N(2)–C(22) | 1.474(5) | N(2)–C(22) | 1.273(4) | N(2)–C(22) | 1.450(4) |
| | | P(1)–O(1) | 1.456(3) | P(1)–O(1) | 1.488(3) | C(20)–C(21) | 1.434(5) |
| P(2)–Ru(1)–P(3) | 97.95(3) | P(2)–Ru(1)–P(3) | 98.35(4) | P(2)–Ru(1)–P(3) | 98.1(1) | P(1)–Ru(1)–P(2) | 102.3(1) |
| P(2)–Ru(1)–N(1) | 167.97(8) | P(2)–Ru(1)–N(1) | 167.4(3) | P(2)–Ru(1)–N(1) | 165.3(2) | P(1)–Ru(1)–N(1) | 90.5(2) |
| P(2)–Ru(1)–N(2) | 88.9(1) | P(2)–Ru(1)–N(2) | 89.1(1) | P(2)–Ru(1)–N(2) | 86.7(1) | P(1)–Ru(1)–N(2) | 165.5(3) |
| P(2)–Ru(1)–Cl(1) | 89.6(3) | P(2)–Ru(1)–Cl(1) | 89.5(1) | P(2)–Ru(1)–Cl(1) | 87.4(1) | P(1)–Ru(1)–Cl(1) | 86.9(1) |
| P(2)–Ru(1)–Cl(2) | 95.1(1) | P(2)–Ru(1)–Cl(2) | 94.5(1) | P(2)–Ru(1)–Cl(2) | 103.0(1) | P(1)–Ru(1)–Cl(2) | 101.9(1) |
| P(3)–Ru(1)–N(2) | 172.3(1) | P(3)–Ru(1)–N(2) | 171.6(1) | P(3)–Ru(1)–N(2) | 174.6(1) | P(2)–Ru(1)–N(1) | 166.5(1) |
| P(3)–Ru(1)–Cl(2) | 89.5(1) | P(3)–Ru(1)–Cl(2) | 90.5(4) | P(3)–Ru(1)–Cl(2) | 87.5(1) | P(2)–Ru(1)–Cl(2) | 87.4(1) |
| Cl(2)–Ru(1)–N(1) | 85.7(1) | Cl(2)–Ru(1)–N(1) | 85.9(5) | Cl(2)–Ru(1)–N(1) | 81.6(4) | Cl(2)–Ru(1)–N(1) | 85.7(1) |
| Cl(2)–Ru(1)–N(2) | 86.3(1) | Cl(2)–Ru(1)–N(2) | 85.0(2) | Cl(2)–Ru(1)–N(2) | 89.1(1) | Cl(2)–Ru(1)–N(2) | 85.7(1) |
| Cl(2)–Ru(1)–Cl(1) | 165.9(1) | Cl(2)–Ru(1)–Cl(1) | 166.3(1) | Cl(2)–Ru(1)–Cl(1) | 168.2(1) | Cl(2)–Ru(1)–Cl(1) | 170.2(1) |
| N(1)–C(1)–C(2) | 114.7(3) | N(1)–C(19)–C(18) | 114.4(3) | N(1)–C(19)–C(18) | 114.4(3) | N(1)–C(20)–C(21) | 115.9(3) |
| N(2)–C(22)–C(23) | 108.9(3) | N(2)–C(22)–C(23) | 112.0(4) | N(2)–C(22)–C(23) | 127.3(3) | N(2)–C(21)–C(20) | 116.1(3) |

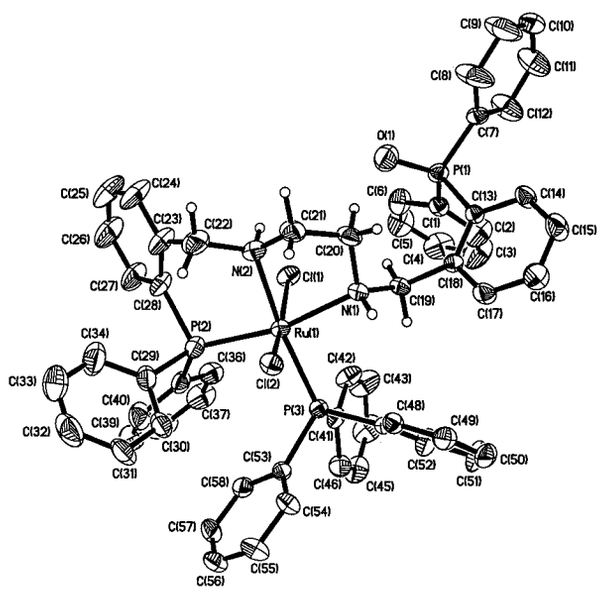



**Fig. 2** A perspective drawing of compound **4**, with the atoms shown at the 30% probability level. Hydrogen atoms of all phenyl rings are omitted for clarity.

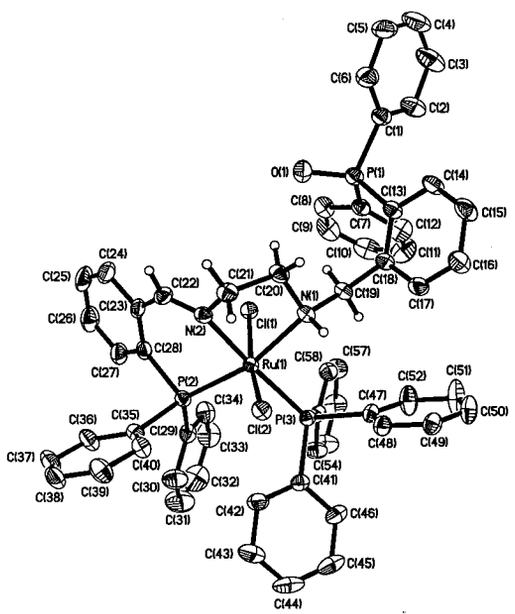



**Fig. 3** A perspective drawing of compound **5**, with the atoms shown at the 30% probability level. Hydrogen atoms of all phenyl rings are omitted for clarity.

consistent with its solid-state structure, exhibiting two doublets and a singlet at $\delta$ 47.4 (d, $^2J_{PP}$ = 28.5 Hz), 38.5 (d, $^2J_{PP}$ = 28.5 Hz) and 29.2 (s) for P(2), P(3) and P(1), respectively.

When reacted with one equivalent of $H_2O_2$, **4** could be further oxidized to form *trans*-$RuCl_2(PPh_3)(\kappa^3\text{-}L^4)$ **5**, whose structure was ascertained by X-ray crystallography (Fig. 3). Selected bond lengths and bond angles are given in Table 1. Structural analysis revealed that the amino group *trans* to the $PPh_3$ group is oxidized to an imino group. The N(1)–C(19) and N(2)–C(22) distances of 1.483(4) and 1.273(4) 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 and a Cl(1)–Ru(1)–Cl(2) angle of 168.2(1)°. The Ru–N distances [Ru–N(1) 2.228(2), Ru–N(2) 2.073(3) 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(1)–P(2) 2.273(1) Å] is shorter than that of the $PPh_3$ group [Ru(1)–P(3) 2.357(1) Å]. This may be a reflection of the chelate effect as well as the *trans* influence. The solid-state structure is consistent with the $^{31}P$, $^1H$ and $^{13}C$ NMR, IR and MS data. The $^{31}P\{^1H\}$ NMR spectrum of **5** exhibits two doublets and a singlet at $\delta$ 55.5 (d, $^2J_{PP}$ = 29.1 Hz), 32.2 (d, $^2J_{PP}$ = 29.1 Hz) and 30.1 (s), which can be assigned to P(2), P(3) and P(1), respectively. The presence of the imino group is supported by the $^1H$ and $^{13}C\{^1H\}$ NMR, and IR spectra. Compound **5** shows a singlet at $\delta$ 8.60 (1H, s) for the proton and a singlet at $\delta$ 169.9 (s) for the carbon of the –CH=N– group in its $^1H$ and $^{13}C\{^1H\}$ NMR spectra, respectively, and $\nu_{C=N}$ at 1631 $cm^{-1}$ in its IR spectrum. The positive FAB mass spectrum exhibits the molecular ion peak $(M + 1)^+$ at *m/z* 1056. In this oxidizing step, only one C–N bond was oxidized to a C=N bond.

When reacted with an excess of $NaBH_4$ in ethanol, **1** was reduced to **3** in high yield.[5] However, when treated with excess $H_2O_2$, **3**, instead of converting back to **1**, was oxidized to a blue species, *trans*-$RuCl_2(\kappa^4\text{-}L^5)$ **6**, whose structure was also ascertained by X-ray crystallography (Fig. 4). Selected bond lengths

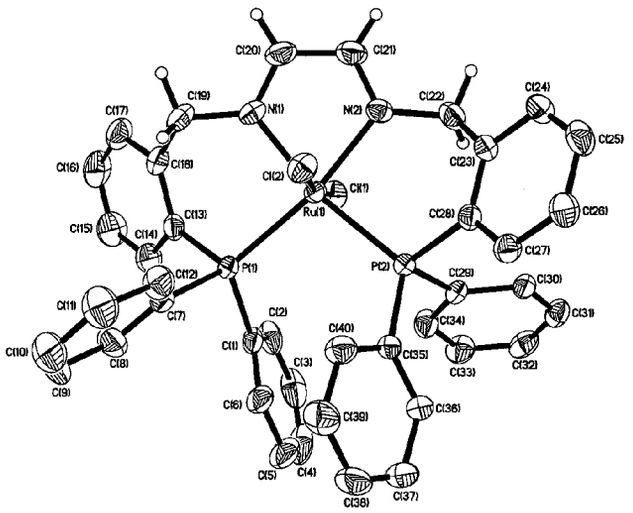



**Fig. 4** A perspective drawing of compound **6**, with the atoms shown at the 30% probability level. Hydrogen atoms of all phenyl rings are omitted for clarity.

and bond angles are given in Table 1. Structural analysis revealed that the [–N(H)$CH_2CH_2$N(H)–] diamino moiety is oxidized to a conjugated (–N=CHCH=N–) diimino moiety. The N(1)–C(20) and N(2)–C(21) distances of 1.294(4) and 1.284(4) Å are consistent with carbon–nitrogen double bonds. The C(20)–C(21) distance [1.434(5) Å] is slightly shorter than a normal carbon–carbon single bond, which is as expected for a conjugated (–N=CHCH=N–) diimino moiety. Other than the diimino moiety, the structure of **6** is very similar to that of *trans*-$RuCl_2(\kappa^4\text{-}L^1)$ **1**.[3] The Ru atom adopts a slightly distorted octahedral geometry with a *trans*-$RuCl_2$ arrangement and a Cl(1)–Ru(1)–Cl(2) angle of 170.2(1)°. The Ru–N [Ru(1)–N(1) 2.050(2), Ru(1)–N(2) 2.048(2) Å] and Ru–P [Ru(1)–P(1) 2.345(1), Ru(1)–P(2) 2.332(1) Å] distances of **6** are slightly shorter than the Ru–N [Ru–N, 2.094(9) and 2.097(6) Å] and slightly longer than the Ru–P [Ru–P, 2.292(2) and 2.298(3) Å] distances of **1**, respectively.[5] This is a reflection of the *trans* influence and the fact that a conjugated diimino group is a better π-acceptor than an isolated imino group. The solid-state structure is consistent with the $^{31}$P, $^{1}$H and $^{13}$C NMR, IR and MS data. The $^{31}$P{$^{1}$H} NMR spectrum of **6** exhibits a singlet at $\delta$ 36.9 (s), which indicates the two phosphorus atoms are equivalent. The presence of the imino group is supported by the $^{1}$H and $^{13}$C{$^{1}$H} NMR, and IR spectra. Compound **6** shows a singlet at $\delta$ 8.35 (s) for the proton and a singlet at $\delta$ 158.8 (s) for the carbon of the (–N=CHCH=N–) moiety in its $^{1}$H and $^{13}$C{$^{1}$H} NMR spectra, respectively, and $\nu_{C=N}$ at 1621 $cm^{-1}$ in its IR spectrum. The positive FAB mass spectrum exhibits the molecular ion peak $(M + 1)^+$ at *m*/*z* 778.

### Catalytic oxidation

The catalytic activities of compounds **1**–**5** to oxidize organic substrates with air have been examined. The results of the catalytic studies are summarized in Tables 2 and 3. Control experiments showed that oxidation of the organic substrates did not occur in the absence of the ruthenium complexes. Table 2 shows that at 80 °C, compounds **1**–**5** were all capable of catalyzing the oxidation of styrene to benzylaldehyde and styrene oxide with air. The oxidations were non-selective, such that both epoxidation and oxidative cleavage of C=C bonds were observed. The ratio of benzylaldehyde to styrene oxide was approximately 1 : 1 in all cases. Compound **2** showed the highest activity, with a conversion of 92% and a turnover frequency (TOF) of 1336. When we monitored the activity of **2** as a function of time, we found that the catalytic activity was preceded by an induction period of about 3 h. The formation of the products was not observed, even after 2.5 h, and a conversion of only 0.32% was observed after 3.5 h. Then, a marked increase in catalytic activity was observed, with an overall conversion of 92% after 16 h. A similar observation was reported by Drago for the catalytic oxidation of norbornene with $O_2$ using *cis*-$[Ru(dmp)_2(CH_3CN)_2](PF_6)_2$ (dmp = 2,9-dimethyl-1,10-phenanthroline).[20] Drago proposed that the incubation period was due to the formation of a ruthenium peroxo norbornyl radical, which led to the formation of epoxide, alcohol and ketone. It is very likely that a similar mechanism is operative for **2**. When the catalytic reaction was carried out in the presence of a 100-fold excess of benzoquinone (a radical trap), no conversion was observed, even after 24 h. This supports the hypothesis that free radicals are present in the catalytic system. The reaction temperature, as well as the steric hindrance of the substituents on the aryl alkene, affects the catalytic activity of **2**. At 120 °C, **2** showed a higher activity; the conversion increased to 99%, the TOF increased to 2024 and the ratio of benzylaldehyde to styrene oxide changed to approximately 1 : 2; however, at temperatures below 40 °C, no catalytic oxidation of styrene was observed. The activity of the catalytic oxidation of aryl alkenes decreases as the size of the substitutents on the olefin increases. Thus, the conversion of α-methylstyrene to acetophenone and 2-phenylpropionaldehyde was only 26% (Table 3, entry 2), and no conversion was observed for *trans*-stilbene (Table 3, entry 3). The catalytic oxidation of **2** toward other organic substrates was also examined. Table 3 shows that **2** was able to catalyze the oxidation of *p*-tolualdehyde to 4-methylbenzoic acid (entry 4), 2-octanol to 2-octanone (entry 5) and benzyl alcohol to benzyl benzoate (entry 6).

The catalytic activity of **2** to oxidize organic substrates with *tert*-butyl hydroperoxide (TBHP) has also been studied (Table 4). In control experiments, no oxidized product was detected in the absence of either **2** or TBHP. Compound **2** catalyzed the oxidation of styrene with TBHP to benzylaldehyde and styrene oxide (approximately 2 : 1 ratio, entry 1). However, with non-aryl alkene, the oxidations were more selective and proceeded mainly *via* epoxidation, with a much lower conversion. *cis*-Cyclooctene was oxidized to 9-oxabicyclo[6.1.0]nonane (entry 2) and norbornene to 2,3-epoxynorbornane (entry 3). Cyclohexene was oxidized to a mixture of 2-cyclohexen-1-ol and 2-cyclohexen-1-one (entry 4), however, the reaction was suppressed in the presence of 2,6-di-*tert*-butyl-4-methylphenol (entry 5). The observations that allylic oxidation was dominant over epoxidation and radical scavengers such as 2,6-di-*tert*-butyl-4-methylphenol suppressed the oxidation suggest that the catalytic reactions involve a free radical intermediate. This notion was further scrutinized by employing cumylhydroperoxide (CHP) as a mechanistic probe—cumyloxyl radical, once formed, will undergo facile β-scission to form acetophenone and a methyl radical.[21] When CHP was used as the oxidant, cyclohexene was oxidized to a mixture of 2-cyclohexen-1-ol and 2-cyclohexen-1-one with the formation of acetophenone, cumene and 2-phenyl-2-propanol.[22] This strongly supports the hypothesis that the catalytic reaction operates *via* reactive alkoxy radicals. Compound **2** is also an efficient catalyst for the oxidation of alcohol with TBHP. In the presence of two equivalents of TBHP in benzene, **2** catalyzed the oxidation of primary alcohols to their corresponding acid (entry 6) or acid ester (entry 7), secondary alcohols to their corresponding ketones (entry 8 & 9) and phenol to *p*-benzoquinone (entry 10). Minisci *et al*. have reported that Fe(III) porphyrin catalyzes the oxidation of phenol to *p*-benzoquinone by TBHP *via* a free radical mechanism.[23] They found that the addition of pyridine enhanced the production of *p*-benzoquinone by catalyzing the decomposition of the alkylhydroperoxide intermediate. We used a similar strategy to test the involvement of reactive free radical species during catalysis and found that the rate of *p*-benzoquinone formation was higher when triethylamine was added to the reaction mixture (entry 11). This observation is consistent with Minisci's postulate.[23]

**Table 2** Catalytic oxidation of styrene with air using complexes **1**–**5**[a]

| Catalyst | Conv. (%)[b] | TOF/h$^{-1}$[c] | Selectivity (%)[d] | |
|---|---|---|---|---|
| | | | Benzylaldehyde[e] | Styrene oxide[e] |
| **1** | 23 | 320 | 56 | 44 |
| **2** | 92 | 1336 | 52 | 48 |
| | 99[f] | 2024 | 31 | 69 |
| | 0[g] | 0 | 0 | 0 |
| **3** | 25 | 363 | 41 | 59 |
| **4** | 51 | 741 | 51 | 49 |
| **5** | 22 | 319 | 56 | 44 |

[a] The reactions were stirred in air at 80 °C for 16 h with the following conditions: catalyst, 0.001 mmol; styrene, 3 g. [b] Determined by GLC analysis based on the starting substrate using an internal standard. [c] TOF = mol of products/mol of catalyst per hour. [d] Determined by GLC analysis based on the converted substrate using an internal standard. [e] Identified by GC-MS. [f] At 120 °C. [g] At 40 °C.

**Table 3** Catalytic oxidation of organic compounds with air using complex **2** as catalyst[a]

| Entry | Substrate | Conv. (%)[b] | Product[c] | Selectivity (%)[d] |
|---|---|---|---|---|
| 1 | Styrene | 92 | Benzylaldehyde | 52 |
| | | | Styrene oxide | 48 |
| 2 | α-Methylstyrene | 26 | Acetophenone | 57 |
| | | | 2-Phenylpropionaldehyde | 41 |
| 3 | *trans*-Stilbene[e] | 0 | — | 0 |
| 4 | *p*-Tolualdehyde | 57 | 4-Methylbenzoic acid | 99 |
| 5 | 2-Octanol | 5.6 | 2-Octanone | 98 |
| 6 | Benzyl alcohol | 1.6 | Benzyl benzoate | 97 |

[a] The reactions were stirred in air at 80 °C for 16 h with the following conditions: catalyst, 0.001 mmol; organic substrate, 3 g. [b] Determined by GLC analysis based on the starting substrate using an internal standard. [c] Identified by GC-MS. [d] Determined by GLC analysis based on the converted substrate using an internal standard. [e] 3 g of *trans*-stilbene was dissolved in 4 cm$^3$ of *p*-xylene and 0.001 mmol of **2** was added. Then the mixture was stirred at 80 °C for 16 h.

**Table 4** Catalytic oxidation of organic compounds with TBHP using complex **2** as catalyst[a]

| Entry | Substrate | Conv. (%)[b] | Product[c] | Selectivity (%)[d] |
|---|---|---|---|---|
| 1 | Styrene | 84 | Benzylaldehyde | 62 |
| | | | Styrene oxide | 37 |
| 2 | *cis*-Cyclooctene | 29 | 9-Oxabicyclo[6.1.0]nonane | 98 |
| 3 | Norbornylene | 19 | 2.3-Epoxynorbornane | 97 |
| 4 | Cyclohexene | 26 | 2-Cyclohexen-1-ol | 4 |
| | | | 2-Cyclohexen-1-one | 93 |
| 5 | Cyclohexene[e] | 1.9 | 2-Cyclohexen-1-one | 97 |
| 6 | Benzylalcohol | 88 | Benzoic acid | 97 |
| 7 | 3-Methyl-1-butanol | 54 | 3-Methylbutyl 3-methylbutanoate | 95 |
| 8 | 2-Octanol | 96 | 2-Octanone | 96 |
| 9 | Cyclohexanol | 75 | Cyclohexanone | 96 |
| 10 | Phenol | 17 | *p*-Benzoquinone | 94 |
| 11 | Phenol[f] | 28 | *p*-Benzoquinone | 96 |
| 12 | Octane | 4.4 | 2-Octanone | 14 |
| | | | 4-Octanone | 82 |
| 13 | Cyclohexane | 5.3 | Cyclohexanol | 19 |
| | | | Cyclohexanone | 72 |
| 14 | Cyclohexane[g] | 4.9 | Cyclohexanol | 15 |
| | | | Cyclohexanone | 74 |
| | | | Cyclohexyl chloride | 7 |
| 15 | Adamantane | 23 | Adamantan-1-ol | 93 |
| | | | 2-Adamantone | 4 |
| 16 | *n*-Propylbenzene | 18 | 1-Phenyl-1-propanone | 96 |
| 17 | Ethylbenzene | 48 | Acetophenone | 97 |
| 18 | Diphenylmethane | 47 | Benzophenone | 99 |
| 19 | Cumene | 68 | 2-Phenyl-2-propanol | 93 |
| | | | Acetophenone | 5 |
| 20 | 1,3-Diisopropylbenzene | 70 | 2,4-Diisopropylphenol | 93 |

[a] The reactions were stirred under nitrogen at room temperature for 16 h with the following conditions: catalyst, 0.001 mmol; organic substrate, 1.5 mmol; TBHP, 3.2 mmol; solvent, benzene, 3 cm$^3$. [b] Determined by GLC analysis based on the starting substrate using an internal standard. [c] Identified by GC–MS. [d] Determined by GLC analysis based on the converted substrate using an internal standard. [e] 2,6-Di-*tert*-butyl-4-methylphenol (0.35 g, 1.6 mmol) was also added to the reaction mixture. [f] Triethylamine (0.09 mmol) was also added to the reaction mixture. [g] Solvent, benzene–$CCl_4$ 9 : 1.

Furthermore, **2** was capable of catalyzing the oxidation of unactivated saturated C–H bonds with TBHP. Alkanes were oxidized to either their corresponding ketones or alcohols, or a mixture of both. The conversions were low for unsubstituted aliphatic alkanes, ranging from 4.4 to 5.3%. In the presence of two equivalents of TBHP and a catalytic amount of **2**, octane

was oxidized to a mixture of 2-octanone and 4-octanone (entry 12), cyclohexane to cyclohexanol and cyclohexanone (entry 13), and adamantane to adamanta-1-ol and 2-adamantone (entry 15). The fact that oxidation of octane occurred at the secondary C–H bond exclusively, with no detectable products from primary C–H bond oxidation, and adamantane preferentially at the tertiary C–H bond suggests that the alkane oxidations probably proceed *via* a H-atom abstraction pathway with rapid radical recombination. This is further supported by the oxidation of cyclohexane in a 9 : 1 benzene–$CCl_4$ mixture (entry 14), which gave cyclohexanol and cyclohexanone, as well as cyclohexyl chloride. A similar mechanism has been proposed for ruthenium-catalyzed oxidation of alkanes with TBHP.[24] However, the conversions for aryl-substituted alkanes were much higher, ranging from 18 to 70%. Under the same conditions, *n*-propylbenzene was oxidized to 1-phenyl-1-propanone (entry 16), ethylbenzene to acetophenone (entry 17), diphenylmethane to benzophenone (entry 18), cumene to a mixture of 2-phenyl-2-propanol and acetophenone (entry 19), and 1,3-diisopropylbenzene to 2,4-diisopropylphenol (entry 20). The substantial increase in the oxidation reactivity of **2** from octane to 1,3-diisopropylbenzene is consistent with the stability of the radicals generated through H-atom abstraction, *i.e.* aryl-substituted radicals are more stable than unsubstituted radicals. Experimental evidence suggests that free radicals are probably involved in the catalytic oxidation processes.

## Experimental

### General procedures

Unless otherwise stated, all reactions were carried out in an atmosphere of dry nitrogen or *in vacuo*. Solvents were dried by standard procedures, distilled and deaerated prior to use. All chemicals used were of reagent grade, obtained from the Aldrich Chemical Company and, where appropriate, degassed before use. Melting points were taken in sealed capillaries and are uncorrected. The compounds $L^1$, $L^2$,[7] and $RuCl_2(PPh_3)_3$[25] were prepared according to literature methods. Microanalyses were performed by 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. $^1H$ and $^{13}C\{^1H\}$ NMR chemical shifts were referenced to internal deuteriated solvents and then recalculated to TMS ($\delta$ 0.00), $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% $H_3PO_4$. Low resolution mass spectra (LRMS) were obtained on Finnigan MAT SSQ-710 and MAT 95 spectrometers in FAB (positive ion) 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 $^{31}P\{^1H\}$ NMR spectroscopy.

### Preparations

**Synthesis of *trans*-$RuCl_2(PPh_3)(\kappa^3$-$L^2)$ 2.** A solution of $L^2$ (0.060 g, 0.1 mmol) and $RuCl_2(PPh_3)_3$ (0.096 g, 0.1 mmol) in dichloromethane (30 $cm^3$) was stirred at room temperature for 4 h, then the solvent was removed in *vacuo* to give an orange residue which was washed with *n*-hexane (2 × 5 $cm^3$). The residue was purified by column chromatography. When eluting with chloroform, an orange band was obtained from the silica gel column. Removal of the solvent from the orange band gave an orange solid which, upon crystallization in a chloroform–hexane mixture, gave orange crystals of **2**. Yield: 0.087 g, 84%; m.p. 190–191 °C (dec). IR ($cm^{-1}$, in KBr): 3057m, 1568m, 1481m, 1432s, 1188m, 1087m, 975m, 746vs, 695vs and 520vs. NMR ($CDCl_3$): $^{31}P\{^1H\}$, $\delta$ 48.6 (d, $^2J_{P-P}$ = 28.9 Hz, $PPh_2$), 38.9 (d, $^2J_{P-P}$ = 28.9 Hz, $PPh_3$) and −13.3 (s, pendant $PPh_2$); $^{13}C\{^1H\}$, $\delta$ 126.7–141.5 (m), 57.0 (s), 49.2 (s), 31.9 (s) and 22.8 (s); $^1H$, $\delta$ 6.41–7.99 (43H, m, Ph-H), 4.70 (2H, m, PhC$H_2$–), 4.32 (2H, m, PhC$H_2$–), 3.61 (2H, m, –NC$H_2$C$H_2$N–), 3.30 (2H, m, –NC$H_2$C$H_2$N–), 2.80 (1H, m, NH), 2.51 (1H, m, NH) and 7.21 (0.75H, s, $CHCl_3$). Found (calc. for $C_{58}H_{53}N_2P_3Cl_2Ru\cdot 0.75CHCl_3$): C, 61.96 (62.27); H, 5.03 (4.75); N, 2.65 (2.47)%. LRMS (positive FAB) *m*/*z*: 1042 $(M + 1)^+$ for $^{102}Ru$ and $^{35}Cl$.

**Synthesis of *trans*-$RuCl_2(\kappa^4$-$L^2)$ 3.** A solution of **2** (0.035 g, 0.034 mmol) in toluene (20 $cm^3$) was heated under reflux in air for 6 h. After cooling to room temperature, the solution was filtered and evaporated to dryness in *in vacuo* to give an orange residue. The residue was washed with diethyl ether (2 × 5 $cm^3$) and crystallized in a dichloromethane–*n*-hexane mixture to give orange crystals of **3**. Yield: 0.024 g, 92%. The identity of **3** was confirmed by comparing its IR, $^{31}P\{^1H\}$ and $^1H$ NMR, and MS (positive FAB) data with those of an authentic sample of *trans*-$RuCl_2(\kappa^4$-$L^2)$.[5]

**Synthesis of *trans*-$RuCl_2(PPh_3)(\kappa^3$-$L^3)$ 4.** A 30% solution of $H_2O_2$ (0.024 g, 0.212 mmol) was added dropwise to a solution of **2** (0.210 g, 0.202 mmol) in chloroform (30 $cm^3$). The reaction mixture was stirred at room temperature for 12 h before it was filtered. The filtrate was evaporated to dryness *in vacuo* to give a red residue, which was washed with diethyl ether (2 × 5 $cm^3$). Crystallization of the red residue in a chloroform–diethyl ether mixture gave red crystals of **4**. Yield: 0.198 g, 93%; m.p 195–196 °C (dec). IR ($cm^{-1}$, in KBr): 3053m, 1481m, 1434s, 1197s., 1093m, 974m, 747s, 705s and 540s. NMR ($CDCl_3$): $^{31}P\{^1H\}$, $\delta$ 47.4 (d, $^2J_{P-P}$ = 28.5 Hz, $PPh_2$), 38.5 (d, $^2J_{P-P}$ = 28.5 Hz, $PPh_3$) and 29.2 [s, $P(O)Ph_2$]; $^{13}C\{^1H\}$, 126.4–133.6 (m), 49.9 (s), 45.4 (s), 31.4 (s) and 22.5 (s); $^1H$, $\delta$ 6.21–7.70 (43H, m, Ph-H), 4.71 (2H, m, PhC$H_2$–), 4.38 (2H, m, PhC$H_2$–), 3.60 (2H, m, –NC$H_2$C$H_2$N–), 3.12 (2H, m, –NC$H_2$C$H_2$N–), 2.60 (1H, m, NH), 2.30 (1H, m, NH), 7.21 (1H, s, $CHCl_3$), 3.46 (4H, q, $J$ = 6.8 Hz, $CH_3CH_2O$) and 1.15 (6H, t, $J$ = 6.8 Hz, $CH_3CH_2O$). Found (calc. for $C_{58}H_{53}Cl_2N_2OP_3Ru\cdot CHCl_3\cdot C_4H_{10}O$): C, 60.33 (60.38); H, 5.13 (5.11); N, 2.31 (2.24)%. LRMS (positive FAB) *m*/*z*: 1058 $(M + 1)^+$ for $^{102}Ru$ and $^{35}Cl$.

**Synthesis of *trans*-$RuCl_2(PPh_3)(\kappa^3$-$L^4)$ 5.** A 30% solution of $H_2O_2$ (0.027 g, 0.238 mmol) was added dropwise to a solution of **4** (0.210 g, 0.198 mmol) in chloroform (30 $cm^3$). The reaction mixture was stirred at room temperature for 12 h before it was filtered. The filtrate was evaporated to dryness *in vacuo* to give a red residue, which was washed with diethyl ether (2 × 5 $cm^3$). Crystallization of the red residue in a chloroform–pentane mixture gave red crystals of **5**. Yield: 0.199 g, 95%; m.p. 200–201 °C (dec). IR ($cm^{-1}$, in KBr): 3048m, 1631m, 1481m, 1434s, 1186s, 1093m, 757s, 695s and 545s. NMR ($CDCl_3$): $^{31}P\{^1H\}$, $\delta$ 55.4 (d, $^2J_{P-P}$ = 29.1 Hz, $PPh_2$), 32.2 (d, $^2J_{P-P}$ = 29.1 Hz, $PPh_3$) and 30.1 [s, $P(O)Ph_2$]; $^{13}C\{^1H\}$, 169.9 (s), 126.9–134.6 (m), 59.8 (s), 30.9 (s) and 21.6 (s); $^1H$, $\delta$ 8.60 (1H, s, –CH=N–), 6.21–7.52 (43H, m, Ph-H), 4.61 (2H, m, PhC$H_2$–), 4.40 (1H, m, –NC$H_2$C$H_2$N–), 3.60 (1H, m, –NC$H_2$C$H_2$N–), 3.31 (2H, m, –NC$H_2$C$H_2$N–), 2.60 (1H, m, NH), 7.22 (1H, s, $CHCl_3$) and 0.78–1.32 [12H, m(br), $C_5H_{12}$]. Found (calc. for $C_{58}H_{51}Cl_2N_2OP_3Ru\cdot CHCl_3\cdot C_5H_{12}$): C, 61.16 (61.51); H, 5.49 (5.14); N, 2.31 (2.25)%. LRMS (positive FAB) *m*/*z*: 1056 $(M + 1)^+$ for $^{102}Ru$ and $^{35}Cl$.

**Synthesis of *trans*-$RuCl_2(\kappa^4$-$L^5)$ 6.** To a yellow solution of **3** (0.180 g, 0.230 mmol) in a chloroform–ethanol mixture(20 $cm^3$, 1 : 10), an excess of $H_2O_2$ (0.078 g, 0.617 mmol) was added. The progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After stirring at room temperature for 20 h, the reaction mixture turned purple. The solvent was removed to give a purple solid, which was re-dissolved in acetone and chromatographed on a silica gel column. A bright red band and a deep blue band were obtained when eluting with *n*-hexane–ethyl acetate (1 : 1) and ethyl acetate, respectively. Removal of the solvent from the red band gave a small amount of a red solid,

**Table 5** Crystallographic data for compounds **2**, **4**, **5** and **6**

| Compound | | **2**·3CHCl$_3$ | **4**·H$_2$O | **5**·H$_2$O·0.25C$_6$H$_{14}$ | **6**·0.5H$_2$O·0.5CH$_3$OH |
|---|---|---|---|---|---|
| Empirical formula | | $C_{61}H_{56}Cl_{11}N_2P_3Ru$ | $C_{58}H_{55}Cl_2N_2O_2P_3Ru$ | $C_{59.5}H_{56.5}Cl_2N_2O_2P_3Ru$ | $C_{40.5}H_{37}Cl_2N_2OP_2Ru$ |
| Formula weight | | 1401.01 | 1076.92 | 1096.44 | 801.63 |
| Crystal size/mm | | 0.20 × 0.12 × 0.10 | 0.15 × 0.10 × 0.10 | 0.15 × 0.10 × 0.10 | 0.30 × 0.20 × 0.10 |
| Crystal system | | Triclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | | $P\bar{1}$ | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ |
| $a$/Å | | 12.590(1) | 17.813(1) | 14.6405(9) | 20.124(2) |
| $b$/Å | | 12.833(1) | 13.709(1) | 14.7995(9) | 18.343(2) |
| $c$/Å | | 21.502(2) | 22.044(2) | 16.0938(9) | 10.1285(8) |
| $\alpha$/° | | 93.614(2) | 90 | 107.006(1) | 90 |
| $\beta$/° | | 100.712(2) | 104.775(2) | 100.158(1) | 93.719(2) |
| $\gamma$/° | | 104.184(2) | 90 | 112.860(1) | 90 |
| $V$/Å$^3$ | | 3288.0(6) | 5204.8(6) | 2901.5(3) | 3730.8(5) |
| $Z$ | | 2 | 4 | 2 | 4 |
| $D_{calc.}$/g cm$^{-3}$ | | 1.415 | 1.372 | 1.249 | 1.422 |
| $T$/K | | 293 | 293 | 293 | 293 |
| Absorption coefficient/mm$^{-1}$ | | 0.797 | 0.540 | 0.486 | 0.683 |
| $\theta$ range/° | | 1.71–26.00 | 1.77–27.51 | 1.40–27.54 | 2.03–27.51 |
| Reflections collected | | 17759 | 30206 | 17170 | 21471 |
| Independent reflections ($R_{int}$) | | 12575 (0.0244) | 11649 (0.0828) | 12464 (0.0231) | 8307 (0.0281) |
| Goodness-of-fit on $F^2$ | | 0.994 | 0.784 | 0.986 | 1.046 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1$ | 0.0516 | 0.0446 | 0.0427 | 0.0363 |
| | $wR2$ | 0.1450 | 0.0741 | 0.1125 | 0.1030 |
| $R$ indices (all data) | $R1$ | 0.0684 | 0.1449 | 0.0661 | 0.0534 |
| | $wR2$ | 0.1559 | 0.0921 | 0.1244 | 0.1114 |

which was then discarded due to its extremely low yield. Removal of the solvent from the blue band gave a blue solid, which was recrystallized from a chloroform–hexane mixture to give deep blue crystals of **6**. Yield: 0.062 g, 35%; m.p 263–265 °C. IR (cm$^{-1}$, in KBr): 3053m, 1621(br)m, 1507m, 1429s, 1098m, 746m, 695s and 519s. NMR ($CDCl_3$): $^{31}P\{^1H\}$, $\delta$ 36.9 (s, $PPh_2$); $^{13}C\{^1H\}$, 158.8 (s), 127.3–134.8 (m) and 67.8 (s); $^1H$, $\delta$ 8.35 (2H, s, –N=CHCH=N–), 6.98–7.27 (28H, m, Ph-H), 5.13 (4H, s, PhC$H_2$–), 7.21 (0.5H, s, $CHCl_3$) and 1.49 [4H, s(br), $H_2O$]. Found (calc. for $C_{40}H_{34}Cl_2N_2P_2Ru$·0.5$CHCl_3$·2$H_2O$): C, 55.52 (55.73); H, 4.42 (4.41); N, 3.41 (3.21)%. LRMS (positive FAB) $m/z$: 778 $(M + 1)^+$ for $^{102}$Ru and $^{35}$Cl.

### Catalytic studies

**General procedure for catalytic oxidation by air.** A reaction mixture of organic substrate (3.0 g) and catalyst (0.001 mmol) was stirred at 80 °C in air for 16 h. The resultant solution was analysed by GC. The identity of the analytes was verified by GC-MS. Control experiments without the catalyst were performed under identical conditions. The results of the catalytic studies are given in Tables 2 and 3.

**General procedure for catalytic oxidation by TBHP.** A solution of organic substrate (1.5 mmol), TBHP (3.2 mmol) and **2** (1 mg, 0.001 mmol) in benzene (3 cm$^3$) was stirred under nitrogen at room temperature for 16 h. The reaction mixture was then poured slowly into a 10% aqueous $Na_2SO_3$ solution (5 cm$^3$) to destroy any remaining TBHP and the resultant solution was extracted with dichloromethane. The organic layer was separated, dried over anhydrous $Na_2SO_4$ and analysed by GC. The identity of the analytes was verified by GC-MS. Control experiments without either the catalyst or TBHP were performed under identical conditions.

### X-Ray crystallography

Pertinent crystallographic data and other experimental details are summarized in Table 5. Crystals of **2**·3CHCl$_3$, **4**·H$_2$O, **5**·H$_2$O·0.25C$_6$H$_{14}$ and **6**·0.5CH$_3$OH·0.5H$_2$O suitable for X-ray diffraction studies were grown by slow evaporation of **2** in a chloroform–hexane mixture, **4** in an acetone–diethyl ether mixture, **5** in an acetone–hexane mixture and **6** in a methanol–diethyl ether mixture, respectively. The water of crystallization probably came from the solvents, which were not dried prior to use. 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$\alpha$ radiation ($\lambda$ = 0.71073 Å). The collected frames were processed with the software SAINT[26] and an absorption correction was applied (SADABS)[27] to the collected reflections. The structures of all compounds were solved by direct methods (SHELXTL™)[28] and refined against $F^2$ by full matrix least-squares analysis. The presence of voids in the crystal lattices of **4** and **5** is presumably caused by the coincidentally inefficient packing of their respective molecules, which possess numerous bulky phosphino moieties. All non-hydrogen atoms were refined anisotropically. Except for the hydrogen atoms of the solvent molecules in **4**, **5** and **6**, which were not located, all other hydrogen atoms were generated in their idealized positions and allowed to ride on their respective parent carbon atoms.

CCDC reference numbers 169813–169816.

See http://www.rsc.org/suppdata/dt/b1/b106997g/ for crystallographic data in CIF or other electronic format.

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