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Proofs to Prof. M.A. Halcrow,

School of Chemistry, University of Leeds,

Woodhouse Lane, Leeds LS2 9JT, U.K.

Supramolecular Assembly and Transfer Hydrogenation Catalysis with Ruthenium(II) Complexes of 2,6-Di(1*H*-pyrazol-3-yl)pyridine Derivatives

Thomas D. Roberts and Malcolm A. Halcrow*

School of Chemistry, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK

Tel +44 113 343 6506

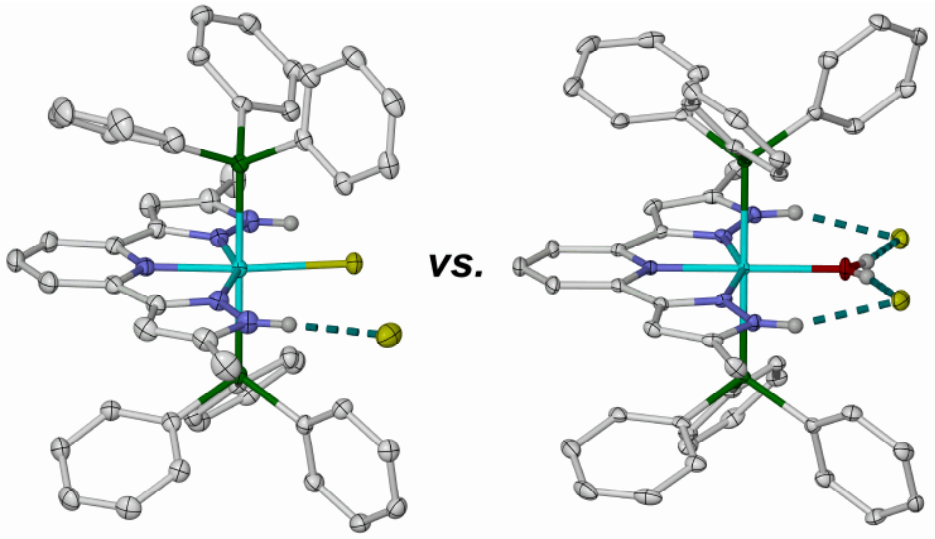
Fax +44 113 343 6565

email m.a.halcrow@leeds.ac.uk

Dedicated to Malcolm Chisholm on the occasion of his 70th birthday.

Submission for the Malcolm Chisholm Special Issue

TOC Entry



Six new complexes of type "[RuCl(PPh$_3$)$_2$(L^R)]Cl" have been prepared, where L^R is a disubstituted 2,6-di(1*H*-pyrazol-3-yl)pyridine derivative. Crystal structures have shown that the chloride ligand in these compounds can be labile under ambient conditions, which is a requirement for catalysis. One complex salt [Ru(OH$_2$)(PPh$_3$)$_2$(L^R)][PF$_6$]$_2$ (R = *t*Bu) was also obtained. All the complexes tested are moderately active towards transfer hydrogenation of acetophenone, with the PF_6^- salt having a much higher activity than the chloride salts.

Keywords

Ruthenium; N-donor ligands; Crystal Structure; Hydrogen Bonding; Transfer Hydrogenation

ABSTRACT

Two new tridentate ligands 2,6-*bis*(5-ethyl-1*H*-pyrazol-3-yl)pyridine and 2,6-*bis*(5-benzamido-1*H*-pyrazol-3-yl)pyridine, have been synthesized. These ligands have been used in a new series of six complexes of formula "$RuCl_2(PPh_3)_2(L^R)\cdot nH_2O$" ($n$ = 1 or 2) where L^R is 2,6-*bis*(5-R-1*H*-pyrazol-3-yl)pyridine (R = Me, Et, *t*Bu, NH_2, NHC{O}*t*Bu and NHC{O}Ph). Crystal structures of $[RuCl(PPh_3)_2(L^{Me})]Cl\cdot MeOH$ and $[Ru(OH_2)(PPh_3)_2(L^{tBu})]Cl_2\cdot 4CDCl_3$ contain six-coordinate complex centers with *trans*-phosphine ligands, and show that the chloride ions can occupy the first or second coordination spheres of the complexes. The latter structure demonstrates that the chloride ions in this type of compound can be labile under ambient conditions, which is an essential pre-requisite for catalytic activity. Anion metathesis yielded $[Ru(OH_2)(PPh_3)_2(L^{tBu})][PF_6]_2$, which was also crystallographically characterized. All the complexes (except air-sensitive $[RuCl_2(PPh_3)_2(L^{NH2})]$) were screened for activity towards transfer hydrogenation of acetophenone in refluxing 2-propanol. The chloride salt catalysts are active but show a significant induction period, which may imply decomposition of the complexes during the reaction. However the activity of the PF_6^- salt is much higher, which shows that competition between chloride and substrate for the metal center is a significant factor in catalysis by these compounds.

INTRODUCTION

Complexes of ligands derived from 2,6-di(pyrazol-3-yl)pyridine (3-bpp, Scheme 1) are finding increasing use [1], in fields as diverse as spin-crossover compounds [2, 3], dye-sensitized solar cells [4], emissive materials [5], metal ion separation [6] and catalysis [7-17]. In the latter regard, a particular feature of 3-bpp derivatives are their relatively acidic pyrazolyl N–H groups, which are in close proximity to a coordinated metal ion. These can participate as second-sphere proton donors during catalytic reactions [11, 18], leading to unusual reactivity towards the reduction of small molecules for example [10]. Hydrogen bonding to these N–H groups could also serve to position a substrate molecule close to the metal reaction center [15, 19].

<Insert Scheme 1 here>

A reaction where 3-bpp-containing catalysts have shown promise [18] is transfer hydrogenation [20]. A number of groups have reported the reaction of $[RuCl_2(PPh_3)_3]$ with $L^{R1,H}$ and $L^{R1,R2}$ derivatives (Scheme 1). Two types of compound are generally obtained from these reactions, namely *trans*-$[RuCl(PPh_3)_2(L^{R1,H})]Cl$ [11, 21], or *cis*-$[RuCl_2(PPh_3)(L^{R1,R2})]$ when $R^2 \neq H$ [12-14]. A dinuclear product with deprotonated pyrazolyl groups, $[Ru_2(PPAr_3)_2(\mu\text{-}Cl)(\mu\text{-}L^{R1,H}\text{–}H)_2]Cl$ (Ar = aryl), was also reported in one case [16]. All these types of complex can be useful pre-catalysts for the transfer hydrogenation of ketones. Notably, it is unclear whether the ligand N–H groups in $L^{R1,H}$ complexes of this type participate Brønsted acid/base centers during the catalysis. On one hand, $[RuCl_2(PPh_3)(L^{R1,R2})]$ complexes ($R^2 \neq H$) are generally more active towards transfer hydrogenation [12-14] than $[RuCl(PPh_3)_2(L^{R1,H})]Cl$ ($R^2 = H$) [11], based on published reports. On the other hand, other catalysts of the *cis*-$[RuCl_2(PPh_3)L]$ type with 1*H*-pyrazolyl 'L' ligand donors have the highest activities of all, and exhibit well-defined protonation/deprotonation cycles at their pyrazolyl group that may contribute to their catalytic performance [14]. Moreover, a DF

calculation of transfer hydrogenation by a $[RuH(L^{R1,H})(PR_3)_2]^+$ center also concluded that protonation of the ketone substrate by the ligand N*H* groups is a low-energy mechanistic pathway [11]. Hence, from the available evidence, the activity of $[Ru(L^{R1,R2})]^{2+}$ fragments towards transfer hydrogenation appears to depend on the steric environment of the metal center, as well as on participation of the tridentate ligand in the reaction.

Since we have access to a number of $L^{R1,R2}$ ligands through our work on iron(II) complexes of 3-bpp and its derivatives [3], we decided to investigate their ruthenium chemistry. We report here $[RuCl(PPh_3)_2(L^{R1,H})]Cl$ complexes of six $L^{R1,H}$ derivatives, including two new ligands that have not been synthesized before (Scheme 2). We were particularly interested in complexes of $L^{R1,H}$ bearing protic R^1 substituents, $L^{NH2,H}$ and $L^{NHCOR3,H}$ (Scheme 1), which could enhance their second sphere coordination properties by formation of chelating hydrogen bonds with a substrate or anion [19]. Crystal structures obtained in this work have shown that the coordination chemistry of "$[RuCl(PPh_3)_2(L^{R1,H})]Cl$" complexes is more varied than has been reported up to now, while a preliminary survey of their activity towards transfer hydrogenation is also described.

<Insert Scheme 2 here>

EXPERIMENTAL

The syntheses of 2,6-di(5-amino-1*H*-pyrazol-3-yl)pyridine ($L^{NH2,H}$, Scheme 1) [19], 2,6-di(5-methyl-1*H*-pyrazol-3-yl)pyridine ($L^{Me,H}$) [22], 2,6-di(5-*tert*-butyl-1*H*-pyrazol-3-yl)pyridine ($L^{tBu,H}$) [19, 21], 2,6-bis(5-{*tert*-butylamido}-1*H*-pyrazol-3-yl)-pyridine ($L^{NHCOtBu,H}$) [19] and $[RuCl_2(PPh_3)_3]$ [23] followed the literature procedures. All other manipulations were carried out in air, using reagent-grade solvents.

Synthesis of 2,6-di(3-oxo-pentanoyl)pyridine. Dimethyl pyridine-2,6-dicarboxylate (1.48 g, 7.6 mmol) and sodium methoxide (1.03 g, 19.0 mmol) were suspended in dry toluene (50 cm^3) under a dry nitrogen atmosphere. Butan-2-one (1.37 g, 19.0 mmol) was then added, and the mixture was stirred for 15 mins at room temperature before being heated at 60 ºC for 12 hrs. The yellow suspension was evaporated to dryness, and the residue was added to a mixture of glacial acetic acid (15 cm^3), water (25 cm^3) and ice (25 g). When the ice had melted the resultant yellow precipitate was recovered by filtration and dried *in vacuo*. Yield 1.37 g, 66 %. Found C, 65.8; H, 6.30; N, 5.15 %. Calcd. from $C_{15}H_{17}NO_4$ C, 65.4; H, 6.22; N, 5.09 %. Electrospray mass spectrum: *m/z* 298.1 ($[Na(L)]^+$). ^{1}H NMR ($CDCl_3$ – spectrum complicated by tautomeric isomerism of the dione groups): δ 0.93-1.37 (m, 6H, CH_2CH_3), 2.35-2.78 (m, 4H, CH_2CH_3), 7.92 (t, 8.1 Hz, 1H, Py H^4), 8.01-8.26 (m, 2H, Py $H^{3/5}$). ^{13}C NMR ($CDCl_3$): δ 9.5 (CH_2CH_3), 32.7 (CH_2CH_3), 96.1 ($COCH_2CO$), 124.1 (Py $C^{3/5}$), 138.1 (Py C^4), 151.8 (Py $C^{2/6}$), 172.0 (Et*C*=O), 199.2 (Py*C*=O).

Synthesis of 2,6-di(5-ethyl-1*H*-pyrazol-3-yl)pyridine ($L^{Et,H}$). 2,6-Di(3-oxo-pentanoyl)pyridine (1.00 g, 3.6 mmol) was dissolved in 7:3 ethanol/acetic acid (50 cm^3). Hydrazine monohydrate (0.54 g, 10.7 mmol) was then added, and the solution was stirred at room temperature for 20 hours. The ethanol was removed, and saturated sodium carbonate solution was added to the residue. The resultant mixture was extracted with chloroform, and the organic layer was washed with brine before being dried over Na_2SO_4 and evaporated to leave a pale yellow solid. The product was recrystallized from methanol/diethyl ether. Found 65.7; H, 6.50; N, 24.5 %. Calcd. for $C_{15}H_{17}N_5 \cdot CH_3OH$ C, 65.7; H, 6.76; N, 24.7 %. Electrospray mass spectrum: *m/z* 290.10 ($[Na(L^{Et,H})]^+$). ^{1}H NMR ($CDCl_3$): δ 1.06 (t, 7.3 Hz, 6H, CH_2CH_3), 2.50 (q, 7.3 Hz, 4H, CH_2CH_3), 6.19 (s, 2H, Pz H^4), 7.11 (d, 7.8 Hz, 2H, Py $H^{3/5}$), 7.37 (t, 7.8 Hz, 2H, Py H^4). ^{13}C NMR ($CDCl_3$): δ 13.5 (CH_2CH_3), 20.9 (CH_2CH_3), 100.9 (Pz C^4), 117.7 (Py $C^{3/5}$), 137.1 (Py C^4), 143.8 (Pz C^5), 148.1 (Pz C^3), 154.5 (Py $C^{2/6}$).

Synthesis of 2,6-bis(5-{phenylamido}-1*H*-pyrazol-3-yl)-pyridine ($L^{NHC\{O\}Ph,H}$). 2,6-Di(5-amino-1*H*-pyrazol-3-yl)pyridine (2.00 g, 8.3 mmol) was suspended in dry acetonitrile (90 cm^3) under a nitrogen atmosphere. Benzoyl chloride (4.00 g, 28.4 mmol) was added, and the mixture was then heated at reflux for 48 hours. The off-white precipitate of $L^{NHC\{O\}Ph,H}$·HCl was collected by filtration, then suspended in a two-phase mixture of chloroform (140 cm^3) and saturated aqueous sodium carbonate (140 cm^3). The mixture was heated at reflux for 2 days. The product formed a white precipitate in the aqueous layer which was filtered, washed with acetone and dried. Yield 0.92 g, 33.0 %. Found 65.1; H, 4.10; N, 21.1 %. Calcd. for $C_{25}H_{19}N_7O_2 \cdot ½H_2O$ C, 65.5; H, 4.40; N, 21.4 %. Electrospray mass spectrum: *m*/*z* 472.20 ($[Na(L^{NHC\{O\}Ph,H})]^+$). ^{1}H NMR ($\{CD_3\}_2SO$): δ 7.35 (s, 2H, Pz H^4), 7.49-7.61 (m, 6H, Ph $H^{3/5}$ and Ph H^4), 7.81 (d, 7.7 Hz, 2H, Py $H^{3/5}$), 7.97 (t, 7.7 Hz, 2H, Py H^4), 8.05 (d, 6.0 Hz, 4H, Ph $H^{2/6}$), 11.1 (vbr s, 2H, N*H*C{O}), 13.0 (vbr s, 2H, Pz N*H*). ^{13}C NMR ($\{CD_3\}_2SO$): δ 95.8 (Pz C^4), 118.4 (Py $C^{3/5}$), 127.7 and 128.3 (Ph $C^{2/6}$ and Ph $C^{3/5}$), 131.6 (Ph C^4), 134.0 (Pz C^5), 138.8 (Py C^4), 141.6 (Ph C^1), 147.3 and 148.0 (Pz C^3 and Py $C^{2/6}$), 164.7 (*C*=O). IR ν(C=O) 1672 cm^{-1}.

Synthesis of $[RuCl(PPh_3)_2(L^{R1,H})]Cl \cdot nH_2O$ (R^1 = Me, 1; R^1 = Et, 2; R^1 = *t*Bu, 3; R^1 = NHC{O}*t*Bu, 4; R^1 = NHC{O}Ph, 5; $R^1 = NH_2$, 6). The same basic method, as described here for $[RuCl(PPh_3)_2(L^{Me,H})]Cl$, was followed for all the complexes in this study. A suspension of $[RuCl_2(PPh_3)_3]$ (0.36 g, 0.4 mmol) and L^1 (0.15 g, 0.4 mmol) in dry dichloromethane (15 cm^3) was stirred for 3 hours at room temperature. This yielded an orange precipitate, which was collected by filtration. Alternatively, the products **3**-**6** were soluble in the reaction mixture, and were precipated from it by careful addition of diethyl ether. In either case, the resultant solids were washed repeatedly with diethyl ether to remove excess PPh_3, then dried *in vacuo*.

For [RuCl(PPh$_3$)$_2$($L^{Me,H}$)]Cl·H$_2$O (**1**·H$_2$O): Yield 0.23 g, 91 %. Found C, 61.9; H, 4.80; N, 7.60; Cl, 7.38 %. Calcd. for $C_{49}H_{43}Cl_2N_5P_2Ru$·H$_2$O C, 61.7; H, 4.76; N, 7.34; Cl, 7.43 %. Electrospray mass spectrum (MeCN): *m*/*z* 638.1 ([RuCl(PPh$_3$)($L^{Me,H}$)]$^+$), 900.2 ([RuCl(PPh$_3$)$_2$($L^{Me,H}$)]$^+$). ^{1}H NMR (CD$_3$OD): δ 2.21 (s, 6H, CH_3), 6.37 (s, 2H, Pz H^4), 7.01 (d, 7.7 Hz, 2H, Py $H^{3/5}$), 7.09-7.35 (m, 31 H, Py H^4 and P{C$_6H_5$}$_3$). ^{31}P NMR (CD$_3$OD): δ 24.4.

For [RuCl(PPh$_3$)$_2$($L^{Et,H}$)]Cl·H$_2$O (**2**·H$_2$O): Yield 0.24 g, 67 %. Found C, 62.2; H, 5.10; N, 7.40; Cl, 7.20 %. Calcd. for $C_{51}H_{47}Cl_2N_5P_2Ru$·H$_2$O C, 62.4; H, 5.03, N, 7.13; Cl, 7.22 %. Electrospray mass spectrum (MeCN): *m*/*z* 928.2 ([RuCl(PPh$_3$)$_2$($L^{Et,H}$)]$^+$). ^{1}H NMR (CD$_3$OD): δ 1.06 (t, 7.6 Hz, 6H, CH$_2$CH_3), 2.56 (q, 7.6 Hz, 4H, CH_2CH$_3$), 6.40 (s, 2H, Pz H^4), 7.00 (d, 7.8 Hz, 2H, Py $H^{3/5}$), 7.08-7.32 (m, 31 H, Py H^4 and P{C$_6H_5$}$_3$). ^{31}P NMR (CD$_3$OD): δ 24.4.

For [RuCl(PPh$_3$)$_2$($L^{tBu,H}$)]Cl·2H$_2$O (**3**·2H$_2$O): Yield 0.29 g, 77 %. Found C, 61.9; H, 5.40; N, 6.30; Cl, 6.80 %. Calcd. for $C_{55}H_{55}Cl_2N_5P_2Ru$·2H$_2$O C, 62.5; H, 5.63; N, 6.63; Cl, 6.71 %. Electrospray mass spectrum (MeCN): *m*/*z* 984.3 ([RuCl(PPh$_3$)$_2$($L^{tBu,H}$)]$^+$). ^{1}H NMR (CDCl$_3$): δ 1.14 (s, 18H, C{CCH_3}$_3$), 6.30 (s, 2H, Pz H^4), 6.92 (d, 7.9 Hz, 2H, Py $H^{3/5}$), 7.01-7.18 (m, 31 H, Py H^4 and P{C$_6H_5$}$_3$), 12.05 (br s, 2H, NH). ^{31}P NMR (CDCl$_3$): δ 23.7.

For [RuCl(PPh$_3$)$_2$($L^{NHC\{O\}tBu,H}$)]Cl·H$_2$O (**4**·H$_2$O): Yield 0.11 g, 27 %. Found C, 60.5; H, 5.30; N, 9.20; Cl, 6.10 %. Calcd. for $C_{57}H_{57}Cl_2N_7O_2P_2Ru$·H$_2$O C, 60.9; H, 5.29; N, 8.72; Cl, 6.31 %. Electrospray mass spectrum (dmso): *m*/*z* 886.2 ([RuCl(PPh$_3$)(OSMe$_2$)($L^{HC\{O\}Ph,H}$)]$^+$). ^{1}H NMR (CDCl$_3$): δ 1.25 (s, 18H, C{CCH_3}$_3$), 7.20 (s, 2H, Pz H^4), 7.22-7.46 (m, 24H) and 7.54-7.97 (m, 9H, Py $H^{3/5}$, Py H^4 and P{C$_6H_5$}$_3$). ^{31}P NMR (CDCl$_3$): δ 34.8. IR ν(C=O) 1645 cm^{-1}.

For [RuCl(PPh$_3$)$_2$($L^{NHC\{O\}Ph,H}$)]Cl·H$_2$O (**5**·H$_2$O): Yield 0.25 g, 59 %. %. Found C, 63.3; H, 4.30; N, 8.70 %. Calcd. for $C_{61}H_{49}Cl_2N_7O_2P_2Ru$·H$_2$O C, 62.9; H, 4.42; N, 8.42 %. Electrospray mass spectrum (dmso): *m*/*z* 663.2 ([Ru(OH$_2$)$_2$(OSMe$_2$)($L^{HC\{O\}Ph,H}$–H)]$^+$), 680.5 ([RuCl(OH$_2$)(OSMe$_2$)($L^{HC\{O\}Ph,H}$)]$^+$), 697.3 ([RuCl$_2$(OSMe$_2$)($L^{HC\{O\}Ph,H}$–H)]$^+$). ^{1}H NMR

($CDCl_3$): δ 7.20 (s, 2H, Pz H^4), 7.22-7.46 (m, 24H) and 7.54-7.97 (m, 9H) (Py $H^{3/5}$, Py H^4 and P{C_6H_5}$_3$), 7.70 (t, 7.7 Hz, 1H, Py H^4), 7.79 (d, 7.7 Hz, 2H, Py $H^{3/5}$). ^{31}P NMR ($CDCl_3$): δ 36.5. IR ν(C=O) 1681 cm^{-1}.

For [RuCl(PPh_3)$_2$($L^{NH2,H}$)]Cl·2H_2O (**6**·2H_2O): Yield 0.13 g, 35 %. Found C, 57.6; H, 4.30; N, 10.2; Cl, 7.50 %. Calcd. for $C_{47}H_{41}Cl_2N_7P_2Ru$·2H_2O C, 58.0; H, 4.66; N, 10.1; Cl, 7.28 %. Electrospray mass spectrum (MeCN): *m*/*z* 657.5 ([RuCl(PPh_3)(OH_2)($L^{NH2,H}$)]$^+$), 680.5 ([RuCl(PPh_3)(NCMe)($L^{NH2,H}$)]$^+$). ^{1}H NMR ($CDCl_3$): δ 5.05 (br s, 4H, NH_2), 5.35 (s, 2H, Pz H^4), 6.84-7.09 (m, 18H) and 7.33-7.70 (m, 17H) (Py $H^{3/5}$, Py H^4 and P{C_6H_5}$_3$). ^{31}P NMR ($CDCl_3$): δ 29.1.

Synthesis of [Ru(OH_2)(PPh_3)$_2$($L^{tBu,H}$)][PF_6]$_2$·H_2O (7·H_2O)

A mixture of **3**·2H_2O (0.10 g, 0.1 mmol) and $AgPF_6$ (0.05 g, 0.2 mmol) in dichloromethane (15 cm^3) was stirred for 1 hour at room temperature. The white AgCl precipitate was then removed by filtration, and the filtrate evaporated to dryness. Yield 0.11 g, 91 %. Found C, 51.6; H, 4.40; N, 5.30 %. Calcd. for $C_{55}H_{57}F_{12}N_5OP_4Ru$·$H_2O$ C, 51.8; H, 4.66; N, 5.49 %. ^{1}H NMR (CD_3OD): δ 1.22 (s, 18H, C{CCH_3}$_3$), 6.53 (s, 2H, Pz H^4), 7.03-7.35 (m, 33H, Py $H^{3/5}$, Py H^4 and P{C_6H_5}$_3$). ^{31}P NMR (CD_3OD): δ 23.9 (s, *P*Ph_3), –144.6 (hept, 751 Hz, *P*F_6^-).

Single crystal *X*-ray structure determinations

Single crystals of [RuCl(PPh_3)$_2$($L^{Me,H}$)]Cl·MeOH (**1**·MeOH) and [Ru(H_2O)$_x$(NCMe)$_{1-x}$(PPh_3)$_2$($L^{tBu,H}$)][PF_6]$_2$ (**7**) were grown by slow diffusion of di-*iso*propyl ether into solutions of the complexes in methanol and acetonitrile, respectively. Crystals of [Ru(OH_2)(PPh_3)$_2$($L^{tBu,H}$)]Cl_2·4$CDCl_3$ (**3**·4$CDCl_3$) slowly crystallized from a NMR sample of that compound in $CDCl_3$. Diffraction data were collected with an Agilent Supernova dual-source diffractometer using either monochromated Cu-K_α (λ = 1.54184 Å) or

monochromated Mo-K_α radiation (λ = 0.71073 Å). Experimental details of each structure determination are given in Table 1. The structures were solved by direct methods (*SHELXS97* [24]), and developed by full least-squares refinement on F^2 (*SHELXL97* [24]). Crystallographic figures were prepared using *X-SEED* [25].

<Insert Table 1 here>

***X*-ray structure determination of [RuCl(PPh$_3$)$_2$($L^{Me,H}$)]Cl·MeOH (1·MeOH).** No disorder is present in this structure, and no restraints were applied to the refinement. All non-H atoms were refined anisotropically, while H atoms were placed in calculated positions and refined using a riding model.

***X*-ray structure determination of [Ru(OH$_2$)(PPh$_3$)$_2$($L^{tBu,H}$)]Cl$_2$·4CDCl$_3$ (3·H$_2$O·4CDCl$_3$).** The asymmetric unit contains half a formula unit, with half a complex molecule with Ru(1), N(2), C(5) and O(15) lying on the C_2 axis ¼, *y*, ¼; and, one chloride ion and two chlorofom molecules lying on general positions. No disorder is present in the model, and no restraints were applied during refinement. All non-H atoms were refined anisotropically, while C- and N-bound H atoms were placed in calculated positions and refined using a riding model. The unique H atom on the water ligand, H(15), was located in the Fourier map and allowed to refine, with U_{iso} = 1.5xU_{eq} of O(15).

***X*-ray structure determination of [Ru(H$_2$O)$_x$(NCMe)$_{1-x}$(PPh$_3$)$_2$($L^{tBu,H}$)][PF$_6$]$_2$ (7; *x* = 0.61).** One metal coordination site is occupied by a disordered mixture of water and acetonitrile ligands. This is coupled to disorder in one of the two PF_6^- ions, one of whose orientations is positioned to hydrogen bond to the partial water site. The occupancies of the combined solvent ligand/anion disorder orientations refined to 0.61 (water+anion A):0.39 (acetonitrile+anion B). No restraints were applied to the solvent ligands, but the refined

restraints P–F = 1.57(2) and *trans*-F...F = 3.14(2) Å were applied to the disordered anion. Two phenyl rings on the same PPh_3 ligand are also disordered, over two equally occupied sites which refined successfully without restraints. The phenyl group disorder is driven by a close contact between C(61B) and C(61B^{i}) (symmetry code (i) 1–*x*, *y*, 1.5–*z*), which are 2.07(3) Å apart. To avoid this clash, one molecule in this pair will have the 'A' orientation and the other the 'B' orientation, probably with a random distribution through the crystal. All non-H atoms except the disordered F atoms were refined anisotropically. C- and N-bound H atoms were placed in calculated positions and refined using a riding model. The water H atoms were not located and are not included in the final model, but are accounted for in the density and F(000) calculations. The highest residual Fourier peak (+1.6 $e.Å^{-3}$) and trough (–1.0 $e.Å^{-3}$) are both associated with the PF_6^- ions.

Other measurements.

Elemental microanalyses were performed by the University of Leeds School of Chemistry microanalytical service. ^{1}H, ^{13}C and ^{31}P NMR spectra employed a Bruker DPX300 spectrometer, operating at 300.2, 75.5 and 121.5 MHz respectively. Electrospray mass spectra were obtained on a Bruker MicroTOF spectrometer, from dmso or MeCN feed solutions. The presence of sodium in some molecular ions reflects the use of a $Na[O_2CH]$ calibrant. Diffuse reflectance IR spectra were run using a Perkin Elmer SpectrumOne spectrophotometer. Dry solvents were obtained from the University of Leeds solvent purification service.

Gas chromatograpy analyses were performed using a Bruker 430-GC equipped with a CP-8400 autosampler. Separation was achieved using a BR-5 column (30 m x 0.25 mm (ID) x 0.25 μm film thickness) with carrier gas flow rate of 2.0 cm^3min^{-1}. The temperature ramp from 50 to 310 ^{o}C was 10 $^{o}Cmin^{-1}$ for reactions involving acetophenone, and 20 $^{o}Cmin^{-1}$ for

reactions involving 3,4-dimethoxyacetophenone and 4-nitroacetophenone where better resolution between starting materials and products was observed. The injection volume was 1 μL with a split ratio of 10. The response factors for the standard, substrate and product were calculated using an appropriate calibration for this analyser and column.

RESULTS AND DISCUSSION

The new ligand $L^{Et,H}$ (Scheme 1) was prepared by the usual route for 5',5''-disubstituted 3-bpp derivatives [1, 2, 26]; that is, by a Claisen condensation of dimethyl 2,6-dipicolinate with 2 equiv butan-2-one, followed by treatment of the resultant *bis*-1,3-dione with excess hydrazine. The synthesis of $L^{NHC\{O\}Ph}$ was adapted from our previously published method for $L^{NHC\{O\}tBu}$ [18], by acylation of $L^{NH2,H}$ (Scheme 1) with benzoyl chloride. These, and the other previously reported derivatives $L^{Me,H}$ [22], $L^{tBu,H}$ [19, 21] and $L^{NHCOtBu,H}$ [19], were each reacted with 1 equiv $[RuCl_2(PPh_3)_3]$ to afford complexes of empirical formula "$RuCl_2(PPh_3)_2(L^{R1,H})\cdot nH_2O$" ($R^1$ = Me, **1**; R^1 = Et, **2**; R^1 = *t*Bu, **3**; R^1 = NHC{O}*t*Bu, **4**; R^1 = NHC{O}Ph, **5**; R^1 = NH_2, **6**; Scheme 2). While complex **3** has been described previously [21], the other complexes in this series are new. Bulk samples of **1**-**6** all contain 1 or 2 equiv H_2O by microanalysis (n = 1 or 2). This water, which is also evident by IR spectroscopy, may be lattice solvent and/or part of the ruthenium inner coordination sphere, according to the crystallographic data described below. Hydrated **3**$\cdot 2H_2O$-**6**$\cdot 2H_2O$ are soluble in many organic solvents, including chlorinated solvents which is unusual for a chloride salt of a metal complex. In contrast **1**$\cdot H_2O$ and **2**$\cdot H_2O$, bearing smaller peripheral hydrophobic substituents, only dissolve in polar alcohol solvents. While **1**$\cdot H_2O$ **-5**$\cdot H_2O$ are air-stable, **6**$\cdot 2H_2O$ decomposes in air in the solid state and in solution to one or more ruthenium(III) complex products, as evidenced by a change in color to dark green and a broadening of its NMR

spectrum. That may reflect the influence of the ligand NH_2 substituents, which have a strongly donating resonance contribution and are also readily deprotonated. Both these properties would promote oxidation of the ruthenium center, as observed ($[Fe(L^{NH2,H})_2]^{2+}$ is also air-sensitive, for the same reasons [19]).

Single crystals of two of the above compounds were obtained, which had the following compositions: $[RuCl(PPh_3)_2(L^{Me,H})]Cl\cdot MeOH$ (**1**·MeOH); and $[Ru(OH_2)(PPh_3)_2(L^{tBu,H})]Cl_2\cdot 4CDCl_3$ (**3**·H_2O·$4CDCl_3$). Both complexes exhibit the expected six-coordinate geometry, which is distorted by the narrow $L^{R1,H}$ bite angle of 77-78° (Tables 2 and 3). Notably, the ruthenium coordination sphere in the two structures is different; while **1**·MeOH contains coordinated chloride (Fig. 1), this has been displaced by a water molecule in **3**·H_2O·$4CDCl_3$ (Fig. 2). The complex molecules in **1**·MeOH associate into centrosymmetric hydrogen-bonded dimers through N–H…Cl hydrogen bonding to the chloride ligand; the Cl^- counterions hydrogen bond to the other pyrazolyl N–H groups, and to the methanol solvent (Fig. 1 and Table 4). This mode of association is also found in crystal structures of two other $[RuCl(PPh_3)_2(L^{R1,H})]Cl$ complexes (R^1 = *n*Bu [11] or *t*Bu [21]).

In contrast, crystals of **3**·H_2O·$4CDCl_3$ are composed of discrete $\{[Ru(OH_2)(PPh_3)_2(L^{tBu,H})]Cl_2\cdot 4CDCl_3\}$ assemblies, with both Cl^- ions accepting one N–H…Cl and one O–H…Cl hydrogen bond, and two weaker C–D…Cl interactions from the chloroform solvent (Fig. 2 and Table 4). This strong association of the chloride ions with the complex through second-sphere interactions may explain the unexpected solubility of **3**·$2H_2O$ (and **4**·H_2O-**6**·$2H_2O$) in weakly polar solvents. Such a dicationic structure has not been observed before in complexes of type $[RuCl(PPh_3)_2L]^+$ (L = 2,2':6',2''-terpyridine, $L^{R1,H}$ or another meridional tridentate N-donor ligand) [11, 21, 27]. In particular, the published structure of the same complex, **3**·$2CHCl_3$, has a coordinated chloride ligand [21].

Importantly, the displacement of the chloride ligand by solvent in crystals of **3**·H_2O·$4CDCl_3$ demonstrates that the chloride ligand in **1**-**5** is labile, as required for catalysis. However, in the light of these results, it is unclear whether **2**·H_2O and **4**·H_2O-**6**·$2H_2O$ (which were not crystallized) have $[RuCl(PPh_3)_2(L^{R1,H})]Cl\cdot nH_2O$ or $[Ru(OH_2)(PPh_3)_2(L^{R1,H})]Cl_2\cdot(n-1)H_2O$ formulations in the solid state.

<Insert Figures 1 and 2, and Tables 1-3, here>

Notably, ^1H and ^{31}P NMR spectra of **1**·H_2O -**6**·$2H_2O$ all contain peaks from only a single compound, showing that solvolysis of the chloride ligand is rapid on the NMR timescale. The ^{31}P chemical shifts of the complexes follow the trend:

3 (δ 23.7) < **1** (24.4) = **2** (24.4) < **6** (29.1) < **4** (34.8) < **5** (36.5)

This is broadly consistent with the inductive properties of the ligand R^1 substitutents, with **3** (R^1 = *t*Bu) having the most electron-donating substituents and **5** (R^1 = NHC{O}Ph) the most electron-withdrawing. More electron-donating substituents will increase the basicity of the pyrazolyl N-donor atoms in the $L^{R1,H}$ ligand [28], thus making the Ru centre more electron-rich and shielding the coordinated ^{31}P nuclei. The degree of dissociation of the coordinated chloride in solution, which could vary between the compounds, may also have a bearing on these data however. While strong molecular ions corresponding to the intact complex $[RuCl(PPh_3)_2(L^{R1,H})]^+$ were observed for **1**-**3** by ES-MS, the mass spectra of **4**-**6** were more complicated and showed species of type $[RuCl(solv)(PPh_3)(L^{R1,H})]^+$ or $[RuCl(solv)_2(L^{R1,H})]^+$ (solv = solvent). This suggests $[RuCl(PPh_3)_2(L^{R1,H})]^+$ complexes with heteroatom R^1 substituents may be more labile towards ligand substitution.

The only other $[Ru(solv)(PPh_3)_2L]^{2+}$ (solv = H_2O or MeCN; L = a meridional *tris*-N-donor ligand) complexes to have been crystallographically characterized are salts of more weakly interacting ClO_4^- or PF_6^- anions [29]. Hence, in the light of the above results, **1**·H_2O -**5**·H_2O

were treated with 2 equiv $AgPF_6$ to exchange the chloride ions for more weakly associating PF_6^-. These reactions proved sluggish; significant chloride remained in the materials by microanalysis after reactions at room temperature, while reactions under reflux led to mixtures of products. Only one of the desired cationic products was obtained cleanly by this procedure, namely $[Ru(OH_2)(PPh_3)_2(L^{tBu,H})][PF_6]_2 \cdot H_2O$ (**7**·H_2O). Recrystallization of this material from acetonitrile/di-*iso*propyl ether yielded single crystals of formula $[Ru(OH_2)_x(NCMe)_{1-x}(PPh_3)_2(L^{tBu,H})][PF_6]_2$ ($x \approx 0.6$), in which some of the coordinated water in the crude material had been exchanged by acetonitrile solvent (Fig. 3). Apart from the solvent disorder, the complex cation in the structure of **7** has a similar coordination geometry to the $[Ru(OH_2)(PPh_3)_2(L^{tBu,H})]^{2+}$ center in **3**·H_2O·$4CDCl_3$ (Table 3). The pyrazolyl N–H groups in **7** each donate weaker N–H…F hydrogen bonds to a different PF_6^- ion (Table 4). One of these anions is also disordered, with the major disorder site being positioned to hydrogen bond to the partial water ligand (Fig. 3).

<Insert Figure 3 here>

All the complexes except **6**·$2H_2O$ (because of its air-sensitivity) were screened for activity towards transfer hydrogenation of acetophenone to 1-phenylethanol in refluxing 2-propanol, following a protocol taken from the literature [11]. All the compounds were active although **1**·H_2O-**5**·H_2O exhibited an extended induction period, only giving significant yields (52-81 %) after 24 hrs reaction with a 1 mol% catalyst loading (Table 5). That may indicate that the complexes themselves are inactive, but slowly decompose in the refluxing ethanol to catalytically active ruthenium nanoparticles [30]. Only **5**·H_2O gave a detectable amount of product at shorter reaction times, although reaction for 24 hrs was still required to afford a comparable yield to the other complexes. These data contrast with the literature compound $[RuCl(PPh_3)_2(L^{nBu,H})]Cl$ where, under similar conditions, yields above 90 % were obtained after only 6 hrs reaction with 0.25 mol% catalyst [11]. In contrast, the activity of **7**·H_2O was

much higher, with 60 % conversion being observed after 2 hrs and the reaction being almost complete after 4 hrs (Table 5). Compound **7**·H_2O is a more active catalyst for this reaction than other published [$RuCl(PPh_3)_2(L^{R1,H})$]Cl complexes [11], but it is less active than catalysts of the [$RuCl_2(PPh_3)(L^{R1,R2})$] type [12-14].

<Insert Table 5 here>

Three of the complexes were also screened against two other substrates with inductively donating (3,4-dimethoxyacetophenone) or withdrawing (4-nitroacetophenone) substituents (Table 6). Reactions with 3,4-dimethoxyacetophenone were lower yielding than acetophenone, which is consistent with some previous reports [12, 13], but were also more rapid for two of the complexes. In contrast, 4-nitroacetophenone gave zero or trace product yields with all three of the catalysts examined.

<Insert Table 6 here>

CONCLUSION

Six new complexes of the "[$RuCl(PPh_3)_2(L^{R1,H})$]Cl" type (**1**-**6**) have been prepared. Single crystal structures of two of the compounds had the compositions [$RuCl(PPh_3)_2(L^{R1,H})$]Cl·solv and [$Ru(OH_2)(PPh_3)_2(L^{R1,H})$]$Cl_2$·solv (solv = solvent), demonstrating that the chloride ligand in complexes of this type can be labile under ambient conditions. This is a new observation to our knowledge, that is an essential first step for the activity of these compounds towards catalysis. However, it also means that the precise chemical structures of these complexes are uncertain, since bulk samples of **1**-**6** all contain 1 or 2 equiv of water by microanalysis when isolated under ambient conditions. This water content could be metal-coordinated, or simply included in the crystal lattice, in different compounds. Metathesis of the chloride ions in **1**-**5** using $AgPF_6$ was sluggish, possibly reflecting the supramolecular complexation of Cl^- by the

complexes' N–H donors (Figs. 1 and 2), and only one compound of type $[Ru(solv)(PPh_3)_2(L^{R1,H})][PF_6]_2$ (R^1 = *t*Bu; **7**·H_2O) was obtained in pure form.

All the compounds in this work, except **6**·$2H_2O$ which was not studied, show activity towards transfer hydrogenation of acetophenone in refluxing 2-propanol. The activities of the chloride salts **1**·H_2O-**5**·H_2O were lower than the related literature compound $[RuCl(PPh_3)_2(L^{R1,H})]Cl$ [11], however, and required a significant induction period that may indicate decomposition of the complexes in the refluxing alcohol medium [30]. The reason for this difference is unclear, but it might relate to the presence of water in the (pre)catalyst complexes. Transfer hydrogenation reactions often function well in water [20], and the higher activity of **7**·H_2O shows that water does not poison catalysis in this system (see below). However, the crystal structure of **3**·$4CDCl_3$ suggests that the presence of water might promote second-sphere binding of chloride to the complex, which would then inhibit coordination of the substrate. That suggestion is supported by two further pieces of evidence. First, is the low activity of **1**·H_2O-**6**·$2H_2O$ towards anion metathesis, showing that they retain chloride unusually strongly. Second, is the catalytic activity of **7**·H_2O, which is substantially higher than for **1**·H_2O-**5**·H_2O and for $[RuCl(PPh_3)_2(L^{R1,H})]Cl$. That shows that water is not inimical to catalysis in this system, *per se*, and proves that catalysis is substantially enhanced by removal of chloride ions from the system.

Finally, although our data are preliminary, it is intriguing that **5**·H_2O is the only chloride salt that does not exhibit an extended initiation, although its catalysis is still slow. That may indicate that the introduction of additional hydrogen bonding groups to the periphery of "$[RuCl(PPh_3)_2(L^{R1,H})]Cl$" complexes may enhance their catalyst properties, which was our goal at the outset of this study. Our current work aims to build on these results to design new chloride-free hydrogenation catalysts based on $L^{R1,H}$ supporting ligands.

SUPPLEMENTARY DATA

CCDC 1411237, 1411238 and 1411239 contain the supplementary crystallographic data for **1**·MeOH, **3**·4$CDCl_3$ and **7**, respectively. 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.

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Table 1. Experimental details for the single crystal structure determinations in this work.

	1·MeOH	**3**·H_2O·4$CDCl_3$	**7**
Formula	$C_{50}H_{47}Cl_2N_5OP_2Ru$	$C_{59}H_{61}Cl_{14}N_5OP_2Ru$	$C_{55.78}H_{57.39}F_{12}N_{5.39}O_{0.61}P_4Ru$
M_r	967.84	1515.44	1265.99
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$C2/c$
a (Å)	11.9494(7)	12.1641(5)	41.2547(14)
b (Å)	12.4660(7)	10.8190(4)	12.9487(6)
c (Å)	16.6969(10)	25.7429(10)	21.7812(4)
α (°)	79.907(5)	–	–
β (°)	78.706(5)	91.863(3)	96.097(3)
γ (°)	64.883(6)	–	–
V (Å^3)	2196.5(2)	3386.1(2)	11569.6(7)
Z	2	2	8
T (K)	120(2)	100(2)	110(2)
ρ_{calc} (g.cm^{-3})	1.463	1.486	1.454
μ (mm^{-1})	5.048[a]	0.874[b]	3.953[a]
Measured reflections	17211	15626	25671
Independent reflections	8261	7979	11030
R_{int}	0.034	0.033	0.046
Observed reflections [$I > 2\sigma(I)$]	7254	6455	9133
Data, restraints, parameters	8261, 0, 554	7979, 0, 378	11030, 18, 820
$R_1(I > 2\sigma(I))$[c], wR_2(all data)[d]	0.031, 0.080	0.055, 0.107	0.069, 0.200
GOF	1.025	1.135	1.013
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e.Å^{-3})	–0.73, 0.91	–1.35, 1.65	–1.07, 1.56

[a]Data collected using Cu-K_α radiation. [b]Data collected using Mo-K_α radiation. [c]$R = \Sigma\,[\,|F_o| - |F_c|\,] / \Sigma\,|F_o|$. [d]$wR = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$

Table 2. Selected bond lengths and angles in the crystal structure of **1**·MeOH (Å, º).

Ru(1)–N(2)	1.9888(19)	Ru(1)–Cl(20)	2.4721(5)
Ru(1)–N(9)	2.1100(17)	Ru(1)–P(21)	2.3650(6)
Ru(1)–N(15)	2.0556(18)	Ru(1)–P(40)	2.3906(6)
N(2)–Ru(1)–N(9)	77.75(7)	N(9)–Ru(1)–P(40)	88.88(5)
N(2)–Ru(1)–N(15)	78.42(7)	N(15)–Ru(1)–Cl(20)	92.20(5)
N(2)–Ru(1)–Cl(20)	170.60(5)	N(15)–Ru(1)–P(21)	91.25(5)
N(2)–Ru(1)–P(21)	91.02(6)	N(15)–Ru(1)–P(40)	91.42(5)
N(2)–Ru(1)–P(40)	89.06(6)	Cl(20)–Ru(1)–P(21)	89.799(19)
N(9)–Ru(1)–N(15)	156.16(7)	Cl(20)–Ru(1)–P(40)	90.559(19)
N(9)–Ru(1)–Cl(20)	111.63(5)	P(21)–Ru(1)–P(40)	177.293(18)
N(9)–Ru(1)–P(21)	88.50(5)		

Table 3. Selected bond lengths and angles in the crystal structures of **3**·H_2O·4$CDCl_3$ and **7** (Å, º). The Table is formatted to facilitate comparison of the two structures. Symmetry code: (ii) ½−*x*, *y*, ½−*z*.

3·H_2O·4$CDCl_3$		**7**	
Ru(1)–N(2)	1.979(4)	Ru(1)–N(2)	1.997(4)
Ru(1)–N(7)	2.065(3)	Ru(1)–N(9)	2.097(4)
		Ru(1)–N(18)	2.095(4)
Ru(1)–O(15)	2.148(4)	Ru(1)–O(26A)/N(26B)	2.171(7)/2.125(12)
Ru(1)–P(16)	2.4113(8)	Ru(1)–P(29)	2.4096(11)
		Ru(1)–P(48)	2.4100(12)
N(2)–Ru(1)–N(7)	77.85(8)	N(2)–Ru(1)–N(9)	77.10(16)
		N(2)–Ru(1)–N(18)	77.69(16)
N(2)–Ru(1)–O(15)	180	N(2)–Ru(1)–O(26A)/N(26B)	174.5(2)/173.2(4)
N(2)–Ru(1)–P(16)	90.10(2)	N(2)–Ru(1)–P(29)	88.92(11)
		N(2)–Ru(1)–P(48)	91.24(12)
N(7)–Ru(1)–N(7^{ii})	155.69(16)	N(9)–Ru(1)–N(18)	154.74(15)
N(7)–Ru(1)–O(15)	102.15(8)	N(9)–Ru(1)–O(26A)/N(26B)	98.3(2)/109.4(4)
N(7)–Ru(1)–P(16)	88.50(8)	N(9)–Ru(1)–P(29)	86.97(11)
N(7)–Ru(1)–P(16^{ii})	91.54(8)	N(9)–Ru(1)–P(48)	90.71(11)
		N(18)–Ru(1)–O(26A)/N(26B)	107.0(2)/95.7(4)
		N(18)–Ru(1)–P(29)	91.02(11)
		N(18)–Ru(1)–P(48)	91.38(11)
O(15)–Ru(1)–P(16)	89.90(2)	O(26A)/N(26B)–Ru(1)–P(29)	93.7(2)/89.6(3)
		O(26A)/N(26B)–Ru(1)–P(48)	85.9(2)/90.5(3)
P(16)–Ru(1)–P(16^{ii})	179.79(5)	P(29)–Ru(1)–P(48)	177.58(4)

Table 4. Hydrogen bond parameters for the crystal structures in this work (Å, º). Symmetry code: (i) 1−*x*, 1−*y*, 1−*z*.

	D–H	H…A	D…A	D–H…A
1·MeOH				
N(10)–H(10)…Cl(59)	0.88	2.26	3.119(2)	166.8
N(16)–H(16)…Cl(20^{i})	0.88	2.48	3.316(2)	158.8
O(61)–H(61)–Cl(59)	0.84	2.32	3.126(2)	162.1
3·4$CDCl_3$				
N(8)–H(8)…Cl(35)	0.88	2.31	3.146(3)	159.8
O(15)–H(15A)…Cl(35)	0.88(4)	2.26(4)	3.1281(16)	167(4)
C(36)–H(36)–Cl(35)	1.00	2.63	3.461(4)	140.1
C(40)–H(40)–Cl(35)	1.00	2.40	3.343(4)	157.7
7				
N(10)–H(10)…F(79A)	0.88	2.10	2.952(9)	161.5
N(10)–H(10)…F(79B)	0.88	2.26	3.088(12)	155.8
N(19)–H(19)…F(69)	0.88	2.14	3.019(6)	174.3
O(26A)…F(79A)	–	–	3.140(12)	–

Table 5. Catalysis of the transfer hydrogenation of acetophenone to 1-phenylethanol by the complexes in this work (*iso*-propanol, K[O*i*Pr], 80 °C).

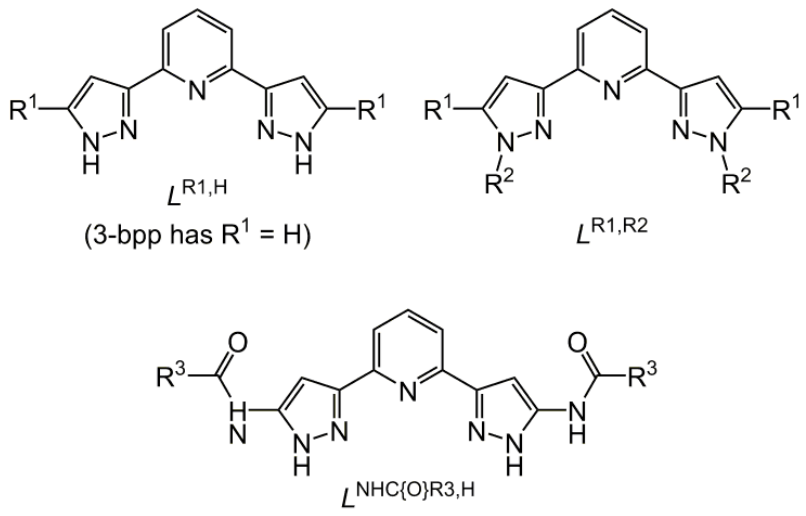
catalyst	loading (mol %)	yield (%)[a] 1 hr		20 hrs
3·2H_2O	0.2	0		0
3·2H_2O	0.5	0		48
3·2H_2O	1.0	0		84
catalyst	loading (mol %)	yield (%)[a] 2 hrs	8 hrs	24 hrs
1·H_2O	1.0	0	0	64
2·H_2O	1.0	0	0	80
3·2H_2O	1.0	0	0	81
4·H_2O	1.0	0	0	52
5·H_2O	1.0	19	32	64
7·H_2O	1.0	59	80[b]	86

[a]Yields by GC analysis. [b]80 % yield observed after 4 hrs reaction.

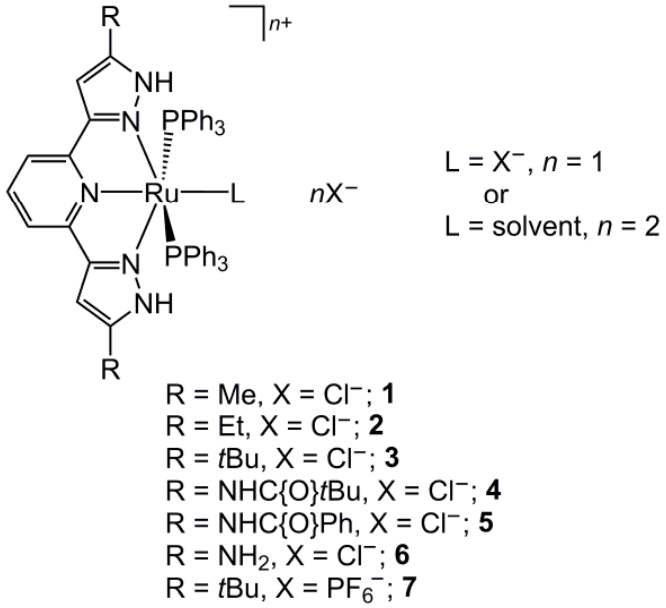
Table 6. Catalysis of the transfer hydrogenation of acetophenone to 1-phenylethanol by the complexes in this work (1 mol% catalyst, *iso*-propanol, K[O*i*Pr], 80 °C).

catalyst	Substrate[a]	yield (%)[b]	
		8 hrs	24 hrs
2·H_2O	**I**	0	80
2·H_2O	**II**	20	18
2·H_2O	**III**	0	0
3·$2H_2O$	**I**	0	81
3·$2H_2O$	**II**	11	30
3·$2H_2O$	**III**	4	4
5·H_2O	**I**	32	64
5·H_2O	**II**	0	27
5·H_2O	**III**	0	0

[a]**I** = acetophenone; **II** = 3,4-dimethoxyacetophenone; **III** = 4-nitroacetophenone. [b]Yields by GC analysis.



Scheme 1. The 3-bpp derivatives referred to in this study.



Scheme 2. The complexes in this work.

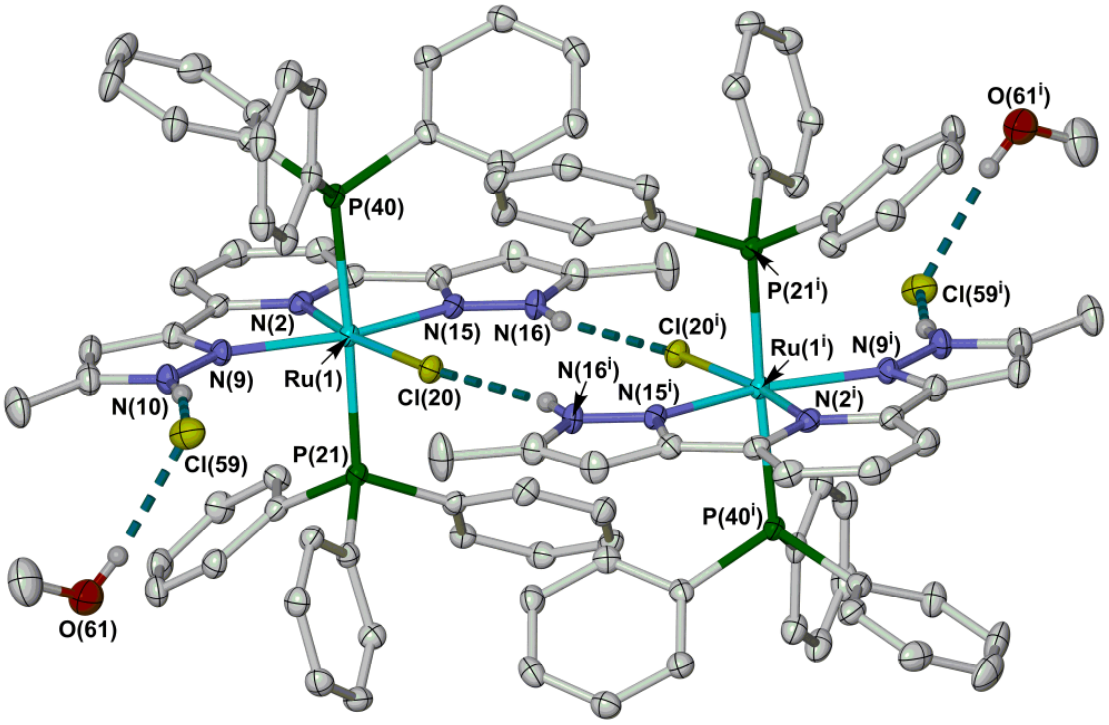


Figure 1 The centrosymmetric assembly of two [RuCl(PPh$_3$)$_2$(L^{tBu})]Cl·MeOH moieties in the crystal structure of **1**·MeOH. Displacement ellipsoids are at the 50 % probability level, and C-bound H atoms are omitted for clarity. Color code: C, white; H, pale gray; Cl, yellow; Fe, cyan; N, blue; P, green; O, red. Symmetry code: (i) 1−*x*, 1−*y*, 1−*z*.

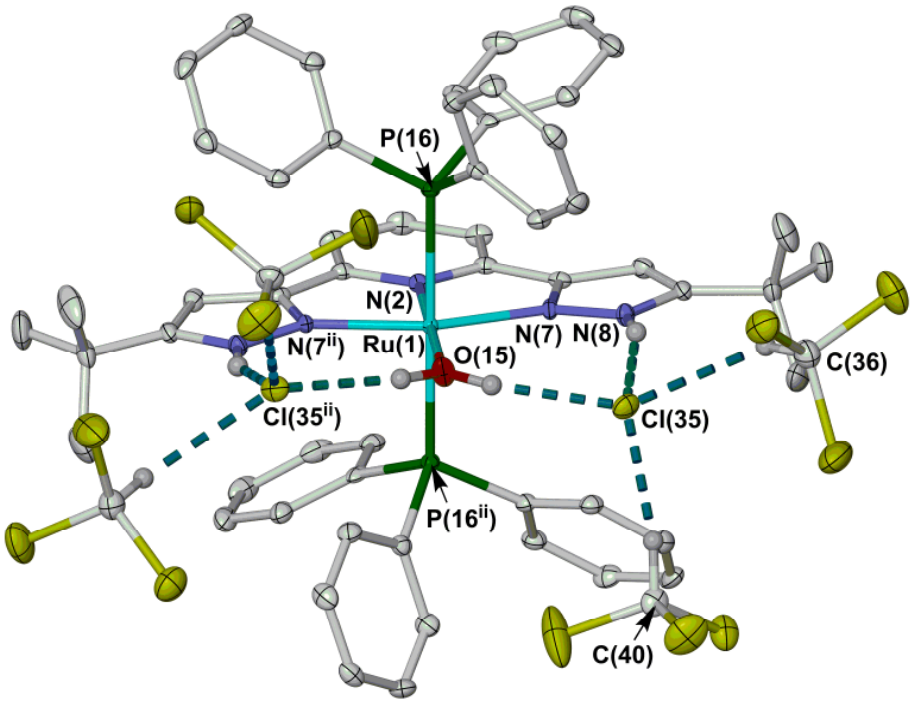


Figure 2 The C_2-symmetric $[Ru(OH_2)(PPh_3)_2(L^{tBu})]Cl_2 \cdot 4CDCl_3$ assembly in the crystal structure of **3**·4$CDCl_3$. Details as for Fig. 1. Symmetry code: (ii) ½−*x*, *y*, ½−*z*.

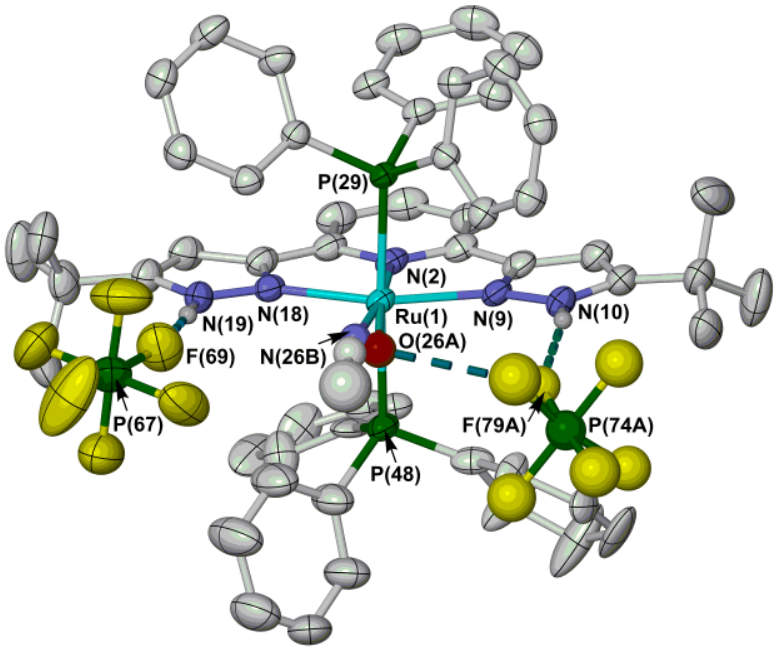


Figure 3 View of the $[Ru(H_2O)_x(NCMe)_{1-x}(PPh_3)_2(L^{Bu})][PF_6]_2$ formula unit in the crystal structure of **6**. The partial water and acetonitrile ligands are both shown, but only one orientation of the disordered phenyl rings and PF_6^- ion is included. Other details as for Fig. 1.