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Supramolecular assembly and transfer hydrogenation catalysis with ruthenium(II) complexes of 2,6-di(1*H*-pyrazol-3-yl)pyridine derivatives

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

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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.

1. 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].

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

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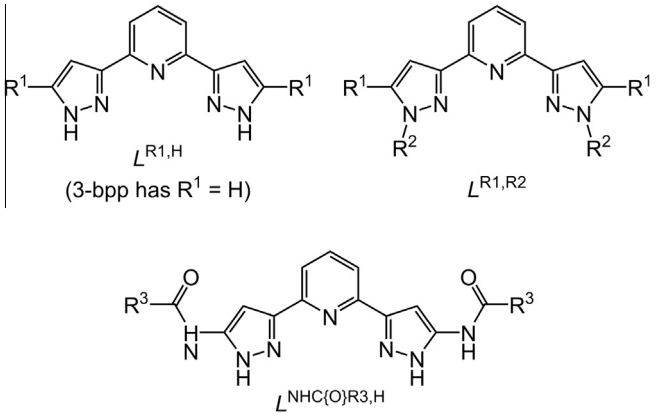


Scheme 1. The 3-bpp derivatives referred to in this study.

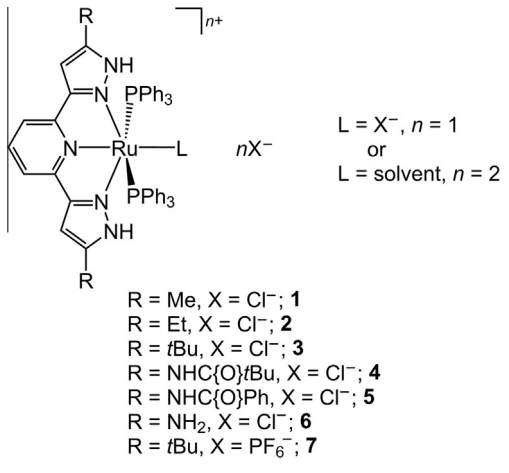
two new ligands that have not been synthesized before (Scheme 2). We were particularly interested in complexes of $L^{R1,H}$ bearing protic R^1 substituents, $L^{NH2,H}$ and $L^{NHCOR3,H}$ (Scheme 1), which could enhance their second sphere coordination properties by formation of chelating hydrogen bonds 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.

2. 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.

2.1. 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 min at room temperature before being heated at 60 °C for 12 h. 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%. *Anal.* Calc. for $C_{15}H_{17}NO_4$: C, 65.4; H, 6.22; N, 5.09. Found: C, 65.8; H, 6.30; N, 5.15%. 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).



Scheme 2. The complexes in this work.

2.2. Synthesis of 2,6-di(5-ethyl-1H-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 h. 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. *Anal.* Calc. for $C_{15}H_{17}N_5{\cdot}CH_3OH$: C, 65.7; H, 6.76; N, 24.7. Found: C, 65.7; H, 6.50; N, 24.5%. 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 $C^{2/6}$).

2.3. Synthesis of 2,6-bis(5-{phenylamido}-1H-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 h. The off-white precipitate of $L^{NHC\{O\}Ph,H}{\cdot}$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%. *Anal.* Calc. for $C_{25}H_{19}N_7O_2{\cdot}1/2H_2O$: C, 65.5; H, 4.40; N, 21.4. Found: C, 65.1; H, 4.10; N, 21.1%. Electrospray mass spectrum: *m*/*z* 472.20 ([Na($L^{NHC\{O\}Ph,H}$)]$^+$). ^{1}H NMR ({CD_3}$_2$SO): 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}$_2$SO): 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}.

2.4. Synthesis of [RuCl(PPh_3)$_2$($L^{R1,H}$)]Cl·nH_2O (R^1 = Me, **1**; R^1 = Et, **2**; R^1 = tBu, **3**; R^1 = NHC{O}tBu, **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 $L^{Me,H}$ (0.15 g, 0.4 mmol) in dry dichloromethane (15 cm^3) was stirred for 3 h 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 precipitated from it by careful