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Backbone-functionalised ruthenium diphosphine complexes for catalytic upgrading of ethanol and methanol to iso-butanol†

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Efficient catalysts for Guerbet-type ethanol/methanol upgrading to iso-butanol have been developed via Michael addition of a variety of amines to ruthenium-coordinated dppe (1,1-bis(diphenylphosphino)ethylene). All catalysts produce over 50% iso-butanol yield with >90% selectivity in 2 h with catalyst **1** showing the best activity (74% yield after this time). The selectivity and turnover number approach 100% and 1000 respectively using catalyst **6**. The presence of uncoordinated functionalised donor groups in these complexes results in a more stable catalyst compared to unfunctionalised analogues.

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Introduction

The gradual move from gasoline to either pure biofuels or biofuel blends is a significant contribution towards environmental sustainability and fuel security.^{1,2} Biomass-derived fuels have attracted increasing attention due to their economic, environmental and societal benefits albeit there is still a lively debate regarding the most sustainable way to deploy such fuels as part of an overall energy portfolio.^{1–4} Bioethanol has long emerged as an alternative to gasoline but is associated with some drawbacks: its energy density is relatively low (around 70% gasoline energy density), it can easily retain water leading to separation and dilution problems in engine tanks and has a proven tendency to corrode existing engine technology and fuel infrastructure.^{5,6} By contrast, higher molecular weight alcohols such as *n*-butanol, possess similar fuel properties to conventional gasoline and are often termed “advanced biofuels”; for example, the energy density of *n*-butanol is about 90% that of gasoline, it is not miscible with water and not corrosive.⁷ The branched isomer iso-butanol has even more compatible fuel properties (98% gasoline energy density) relative to *n*-butanol and with the application of these advanced biofuels many of the ethanol limitations can be overcome.⁸ Butanols can be produced through both biological and

chemical processes. The biological process, ABE fermentation, involves the use of strains of the bacterium *Clostridium acetobutylicum* to produce mixtures of acetone, butanol and ethanol.^{9,10} Though known to be sustainable, there are technological issues associated with the ABE process such as low yield (1–2%), separation issues and the high cost of fermentation substrates (molasses),^{7,11,12} making the bulk synthesis of biobutanol a challenge. On the other hand, the more intensive chemical processes to generate *n*-butanol and iso-butanol via transition metal catalysed hydroformylation/hydrogenation reactions exist but these employ the use of a non-renewable petrochemical feedstock (propylene).^{11,13–16}

Guerbet chemistry has emerged as a promising approach to *n*-butanol production as it can be based on renewable bioethanol.¹⁷ This reaction has been in existence for over a century^{18,19} but has attracted renewed interest in recent years.^{16,20–23} In this reaction, C–C bonds are formed from alcohol substrates by means of so-called “borrowed hydrogen” chemistry.²⁴ The reaction pathway includes dehydrogenation of simple alcohol, base-catalyzed aldol condensation reaction and rehydrogenation of the aldol product.²⁵ Our group^{26–33} and others^{34–49} have been seeking new homogeneous catalysts for ethanol upgrading via Guerbet chemistry. Despite these recent advances, there is still significant scope for further catalyst development.

Despite the growing number of ruthenium–phosphine catalysts (Fig. 1, **I–III**)²⁹ and the interest in related first row transition metal catalysts (**IV**),^{40,41} the small-bite angle bis(diphenylphosphino)methane (dppm) catalyst (**I**) that was among our first reported catalysts remains a benchmark in terms of overall performance for the conversion of ethanol and methanol to iso-butanol (Scheme 1). We were therefore interested in

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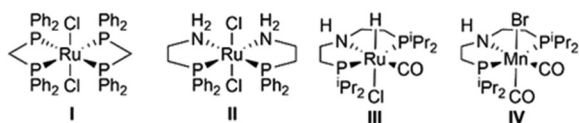
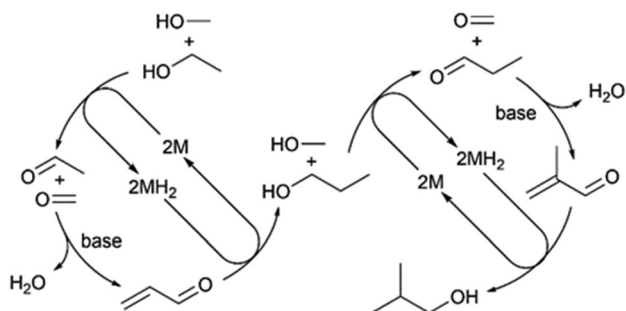


Fig. 1 Previously used ruthenium and manganese phosphine-based catalysts for conversion of ethanol and methanol to iso-butanol.



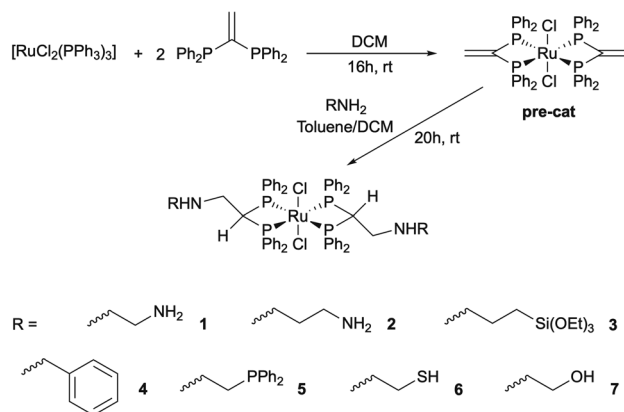
Scheme 1 Catalytic pathway for the Guerbet reaction of ethanol and methanol to iso-butanol.²⁹

expanding this catalyst family, particularly to include pendent functional groups which may improve catalyst solubility in alcohol/water, improve catalyst stability and potentially act as internal bases.

Results and discussion

Synthesis of ruthenium complexes

We identified that Michael-type addition to the commercially available diphosphine 1,1-bis(diphenylphosphino)ethylene (dppen) could be a versatile route to a range of backbone-functionalised ligands with nominally the same bite angle as the parent dppm ligand. Firstly, we synthesised the precursor, *trans*-[RuCl₂(dppen)₂] (**Pre-Cat**) using a literature method^{50,51} and then functionalised with a range of amines to obtain complexes 1–7 (Scheme 2).^{50–53} This route is elegant in that it escapes the need to protect the phosphine moieties, the ruthenium dichloride fragment itself acting as a protecting group (and potentially also activating the olefin towards nucleophilic attack). An alternative approach could be deprotonation of the acidic backbone in dppm complex **I** but this tends to require somewhat forcing conditions and the use of strong bases (^{*n*}BuLi or MeLi).^{54–62} Complexes 1–7 were synthesized as yellow solids in good yields (typically >80%) and characterised by NMR spectroscopy, mass spectrometry and X-ray crystallography. The ³¹P NMR spectrum of the *trans*-[RuCl₂(dppen)₂] (**Pre-Cat**) gave a singlet at 15.3 ppm which upon functionalisation with these amines shifted upfield to *ca.* 11 ppm apart from **6** which gave a peak at 15.9 ppm. In addition to the peak at 11 ppm, **5** displayed another chemical shift at –20.8 ppm corresponding to the uncoordinated pendent PPh₂ group. In



Scheme 2 Synthesis of complexes 1 to 7.

the ¹H NMR spectra, the quintet at 6.1 ppm for the parent *trans*-[RuCl₂(dppen)₂] methylenic proton (C=CH₂) moved to a resonance around 3 ppm in all the complexes, signifying methylene protons along with a newly formed methine proton around 5 ppm. The ESI mass spectra of complexes 1–7 corresponded to the expected chemical structures (see ESI† for further experimental details).

Single crystals of **1**, **3**, **4** and **7** were obtained by slow diffusion of pentane into fluorobenzene/benzene solutions of the complexes. Fig. 2 shows the molecular structures of **1** (a), **3** (b), **4** (c) and **7** (d) with selected bond lengths and angles in Table 1. All crystallographic data are given in the ESI.† All complexes displayed octahedral geometry with *trans* chlorides. The parent complex *trans*-[RuCl₂(dppm)₂] has a P–Ru–P angle of 72°. The analogous angles for **1**, **3**, **4** and **7** are the same within error; similarly, Ru–P and Ru–Cl distances are within the expected range (Table 1).^{51,63,64}

Catalytic activity

Complexes 1–7 were tested for ethanol/methanol to iso-butanol catalysis using the standard conditions we have reported previously;^{28,29} the results are shown in Table 2. In general, all catalysts performed well with over 50% yield and 90% selectivity in 2 h. Catalyst **1** with diamine ethylene functionalities gave 74% yield and 78% ethanol conversion in 2 h (Table 2, run 1). This compares favorably to the previous best catalyst *trans*-[RuCl₂(dppm)₂] (65% yield, 98% selectivity and 88% conversion). Whilst it can be challenging to benchmark more widely against other literature systems where specific attributes (*e.g.* selectivity, TOF) are targeted, this performance is similar to the best existing examples.^{29–33,39,43}

Catalyst **2** with the same amine functionality but a longer propylene linker showed lower activity towards iso-butanol (59% yield). The sequence **1**, **6**, **7** where only the functional group is varied from –NH₂ to –SH to –OH has similar performance for **1** and **7** but catalyst **6** shows exceptionally high selectivity within the liquid phase with iso-butanol being the only product observed by GC. Extending the run time to 20 hours in most cases gave near quantitative conversion of ethanol.



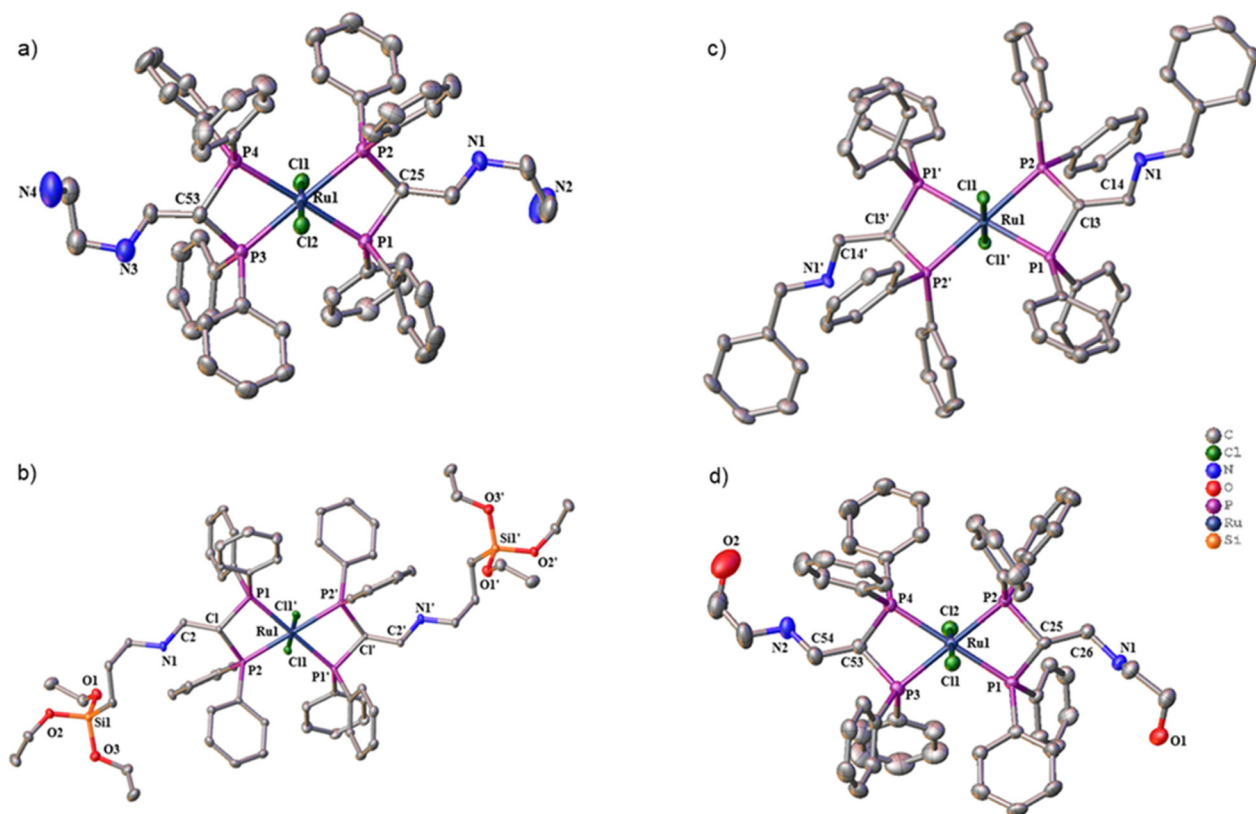


Fig. 2 X-ray crystal structures of complexes **1** (a), **3** (b), **4** (c) and **7** (d) exhibiting *trans*-configurations. Hydrogen atoms and solvent molecules (where present) are omitted for clarity.

Table 1 Selected bond lengths and angles for complexes **1**, **3**, **4** and **7**

Complex **1** crystallises in the triclinic space group $P\bar{1}$. Selected bond lengths (Å): Ru(1)–Cl(1) = 2.4266(12), Ru(1)–Cl(2) = 2.4263(11), Ru(1)–P(1) = 2.3351(12), Ru(1)–P(2) = 2.3722(12), Ru(1)–P(3) = 2.3296(12), Ru(1)–P(4) = 2.3887(12), P(1)–C(25) = 1.861(5), P(2)–C(25) = 1.869(5); Selected bond angles (°): P(1)–Ru(1)–P(2) = 71.81(4), P(2)–Ru(1)–P(4) = 109.04(4), P(1)–C(25)–P(2) = 95.5(2), P(3)–C(53)–P(4) = 96.0(2)

Complex **3** crystallises in the monoclinic space group $P2_1/c$. Selected bond lengths (Å): Ru(1)–Cl(1) = Ru(1)–Cl(1') = 2.4272(3), Ru(1)–P(1) = Ru(1)–P(1') = 2.3409(3), Ru(1)–P(2) = Ru(1)–P(2') = 2.3604(3), P(1)–C(1) = 1.8642(14), P(2)–C(1) = 1.8752(13); Selected bond angles (°): P(1)–Ru(1)–P(2) = P(1')–Ru(1)–P(2') = 71.744(12), P(1)–Ru(1)–P(2) = P(1)–Ru(1)–P(2') = 108.256(12), P(1)–C(1)–P(2) = P(1)–C(1)–P(2') = 94.90(6).

Complex **4** crystallises in the triclinic space group $P\bar{1}$. Selected bond lengths (Å): Ru(1)–Cl(1) = Ru(1)–Cl(1') = 2.4271(8), Ru(1)–P(1) = Ru(1)–P(1') = 2.3731(8), Ru(1)–P(2) = Ru(1)–P(2') = 2.3350(8), P(1)–C(13) = 1.866(3), P(2)–C(13) = 1.862(3) bond angles (°): P(1)–Ru(1)–P(2) = P(1)–Ru(1)–P(2') = 71.06(3), P(1)–Ru(1)–P(2) = P(1)–Ru(1)–P(2') = 108.94(3), P(1)–C(13)–P(2) = P(1)–C(13)–P(2') = 94.44(15).

Complex **7** crystallises in the triclinic space group $P\bar{1}$. Selected bond lengths (Å): Ru(1)–Cl(1) = 2.4232(8), Ru(1)–Cl(2) = 2.4290(8), Ru(1)–P(1) = 2.3504(9), Ru(1)–P(2) = 2.3654(9), Ru(1)–P(3) = 2.3445(9), Ru(1)–P(4) = 2.3717(9), P(1)–C(25) = 1.880(3), P(2)–C(25) = 1.873(3); selected bond angles (°): P(1)–Ru(1)–P(2) = 72.02(3), P(2)–Ru(1)–P(4) = 108.92(3), P(1)–C(25)–P(2) = 95.25(15), P(3)–C(53)–P(4) = 94.74(15)

Any discrepancy between conversion and product yield comes from small amounts of solid byproducts, consisting of a mixture of sodium carbonate, formate and acetate as observed in previous studies.²⁹

The reason for the improved performance of the current catalysts is not definitive at this stage. The obvious reason is a subtle change to catalyst sterics and electronics. We have no NMR spectroscopic evidence for any interaction between the pendent donor groups and ruthenium centre. Some complexes (*e.g.* **1**, **2**, **6**, and **7**) have the possibility for deprotonation

during the basic conditions of catalysis to act as an internal base but other complexes where this is less likely (*e.g.* **3** and **4**) have similar performance. Catalyst **6** with a –SH group has the best performance, certainly in terms of selectivity, suggesting this potentially softer donor group may play an enhanced role in either coordination or deprotonation.

This enhanced stability during catalysis could be due to stabilisation of kinetically fragile intermediates by the pendent groups or, more prosaically, these pendent groups improving catalyst solubility in mixed alcohol/water solvents.

Table 2 Ruthenium catalysed conversion of ethanol and methanol to iso-butanol

$\text{EtOH} + 2 \text{ MeOH} \xrightarrow[2 \text{ NaOMe, 180}^\circ\text{C, 2-20 h}]{0.1 \text{ mol\% Cat}} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 2 \text{ H}_2\text{O}$							
Run ^a	Catalyst	Time (h)	EtOH conversion ^b (%)	Total TON ^c	TON ^d (yield) ^e [selectivity] ^e (%)		
					Iso-butanol	<i>n</i> -Propanol	Hexanols
1	1	2	78	780	740(74)[94]	30(3)[4]	10(1)[1]
2	1	20	80	800	740(74)[94]	40(4)[5]	20(2)[1]
3	2	2	84	840	590(59)[97]	10(1)[2]	10(1)[1]
4	2	20	94	940	690(69)[94]	20(2)[2]	80(8)[4]
5	3	2	83	830	590(59)[97]	10(1)[2]	10(1)[1]
6	3	20	95	950	690(69)[96]	20(2)[2]	40(4)[2]
7	4	2	83	830	600(60)[98]	10(1)[2]	10(1)[1]
8	4	20	95	950	660(66)[96]	20(2)[2]	40(4)[2]
9	5	2	89	890	600(60)[94]	30(3)[5]	10(1)[1]
10	5	20	89	890	680(68)[94]	30(3)[4]	60(6)[3]
11	6	2	88	880	620(62)[100]	0(0)[0]	0(0)[0]
12	6	20	100	1000	790(79)[100]	0(0)[0]	0(0)[0]
13	7	2	79	790	520(52)[97]	20(2)[3]	10(1)[1]
14	7	20	94	940	720(72)[96]	20(2)[2]	40(4)[2]
15	Pre-cat	2	48	480	460(46)[97]	10(1)[2]	10(1)[1]
16 ^f	I	2	88	880	650(65)[98]	12(1)[2]	0(0)[0]

^a Conditions: ethanol (1 mL, 17.13 mmol), methanol (10 mL, 247.13 mmol), [Ru] catalyst (0.01713 mmol, 0.1 mol%), NaOMe (34.26 mmol, 200 mol%), mol% is based on ethanol substrate, 180 °C. ^b Total conversion of ethanol as determined by GC analysis of the liquid phase. ^c Total TON based on mmol of total ethanol converted to products per mmol of [Ru] catalyst (ethanol equivalent relative to mmol of catalysts \times conversion = 1000 \times conversion). ^d TON based on mmol of any product formed per mmol [Ru] catalyst (ethanol equivalent relative to mmol of catalysts \times product yield = 1000 \times product yield). ^e Total yield and selectivity of alcohol products in the liquid fraction as determined by GC. ^f Catalyst I = *trans*-[RuCl₂(dppm)₂].

Conclusions

Backbone-functionalised ligands based on the dppm motif can be accessed by Michael addition of various nitrogen nucleophiles to *trans*-[RuCl₂(dppen)₂], in which the transition metal acts as a protecting group as well as the active catalyst centre. The performance of these complexes as catalysts in the Guerbet upgrading of methanol/ethanol to iso-butanol matches or exceeds that of the parent *trans*-[RuCl₂(dppm)₂], largely due to enhanced stability of these catalysts in standard reaction conditions. This methodology of catalyst derivation has potential to further diversify ligand libraries and offer a potential route to catalyst heterogenisation.

Experimental section

More details of complex synthesis, procedures for performing the catalytic experiments and characterizing data can be found in the ESI.†

General considerations

All procedures were carried out under an inert atmosphere (N₂) using standard Schlenk line techniques or in an inert atmosphere glovebox (Ar). Chemicals were purchased from the usual suppliers and used without further purification. Anhydrous ethanol and methanol were purchased from Sigma-Aldrich and used as received. Pentane and deuterated solvents were dried using established procedures and further degassed

under nitrogen. Other solvents were purified using an Anhydrous Engineering Grubbs-type solvent system.

Synthesis of complexes

Pre-Cat, *trans*-[RuCl₂(dppen)₂], was synthesised using a literature method.^{50,51} Complexes 2–4 have been synthesised previously and were prepared by slight modifications of the literature procedures.^{50,51} Novel complexes 1 and 5–7 were synthesised by adaptations of the same literature method.

Catalysis

Catalytic runs were carried out in a sealed 100 mL Parr stainless steel autoclave with an aluminium heating mantle and using magnetic stirring. A typical procedure using **Pre-Cat** is given below.

Pre-Cat, *trans*-[RuCl₂(dppen)₂], (0.0165 g, 0.0171 mmol, 0.1 mol%), NaOMe (1.85 g, 34.26 mmol, 200 mol%) and a stirrer bar were added to a clean oven dried fitted PTFE insert inside a glove box. The insert was sealed within a 100 mL Parr stainless steel autoclave which was then transferred to a nitrogen/vacuum manifold. Methanol (10 mL, 247.13 mmol) and ethanol (1 mL, 17.13 mmol) were injected into the autoclave through an inlet against a flow of nitrogen. The autoclave was sealed and placed into a pre-heated (180 °C) aluminium heating mantle and stirred at 500 rpm. After the reaction run time (2 h), the autoclave was cooled to room temperature in an ice-water bath. The autoclave was carefully vented to remove any gas generated during the reaction. A liquid sample was



removed, filtered through a short plug of alumina (acidic) and analysed by GC (100 μ L of sample, 25 μ L of hexadecane standard, 1.7 mL diethyl ether – sample filtered through a glass filter paper to remove insoluble salts).

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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