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A ruthenium *cis*-dihydride with 2-phosphinophosphinine ligands catalyses the acceptorless dehydrogenation of benzyl alcohol^{†‡}

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The first ruthenium dihydride complex featuring a phosphinine ligand *cis*-[Ru(H)₂(2-PPh₂-3-Me-6-SiMe₃-PC₅H₂)₂] was synthesised exclusively as the *cis*-isomer. When formed *in situ* from the reaction of *cis*-[Ru(Cl)₂(2-PPh₂-3-Me-6-SiMe₃-PC₅H₂)₂] with two equivalents of Na[BH₃E₃], as demonstrated by ³¹P and ¹H NMR spectroscopy, the catalysed acceptorless dehydrogenation of benzyl alcohol was observed leading to benzyl benzoate in up to 70% yield.

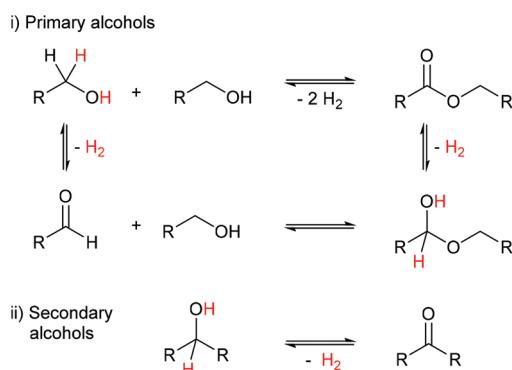
Acceptorless dehydrogenation (AD) is a growing area of significance for hydrogen production and storage, and liquid organic hydrogen carriers (LOHCs) are attractive for hydrogen storage since alcohols can be stored under ambient temperature and pressure.^{1–4} The H₂ that is generated is a clean alternative fuel burning to produce solely water vapour, or H₂ can be utilised in fuel cells.^{5,6} AD has additional applications in chemical synthesis because catalytic AD reactions do not require toxic stoichiometric reagents, thus minimising harmful waste.^{7–9} AD coupling reactions of alcohols can provide a cleaner, more atom efficient synthesis of esters, for example, without the need for acid chloride intermediates.⁷ Esters are used in the production of perfumes, paints and varnishes, and are therefore high value commodities.¹⁰

Alcohols are important starting materials that can be bio-sourced, offering complementary synthetic routes to conventional routes based on fossil-fuel-derived starting materials, although alcohols tend to be quite unreactive.^{11,12} The AD of secondary alcohols leads to ketones, whereas primary alcohols can give aldehydes and esters (Scheme 1). Ru catalysts are important in these processes but can be deactivated by decarbonylation of the aldehydes formed.⁷ Early Ru catalysts for AD include [Ru(OCOCF₃)₂(CO)(PPh₃)₂] alongside an acid promoter,¹³ related ruthenium(II) trifluoroacetate diphosphine com-

plexes,¹⁴ [Ru(H)₂(PPh₃)₄], at 180 °C,^{15,16} and Shvo's catalyst at 145 °C for the conversion of PhCH₂OH to benzyl benzoate.¹⁷

Pioneering studies by Milstein and coworkers have shown that metal-ligand cooperation (MLC), the active participation of the ligand in bond-making and bond-breaking steps in homogeneous catalytic reactions,^{18–21} between a dearomatised pincer ligand and a Ru centre gave highly effective catalysts for ester formation from alcohols.²² For benzyl alcohol at 115 °C, a 92% yield of benzyl benzoate was achieved in 4 h.²² Pincer-ligand systems²³ involving both precious^{10,24–31} and first row^{18,32–38} transition metals have been the focus of recent investigations into AD.

Homogeneous ruthenium catalysts with phosphine ligands have proven extremely useful over many decades including those with the small bite-angle ligand bis(diphenylphosphino-methane) (dppm).³⁹ For example, the pre-catalyst *cis*-[Ru(Cl)₂(dppm)₂] achieved an initial TOF of 180 000 h⁻¹ for the reaction of CO₂ with hydrogen in an amine solution leading to



Scheme 1 Acceptorless dehydrogenation reactions of alcohols.

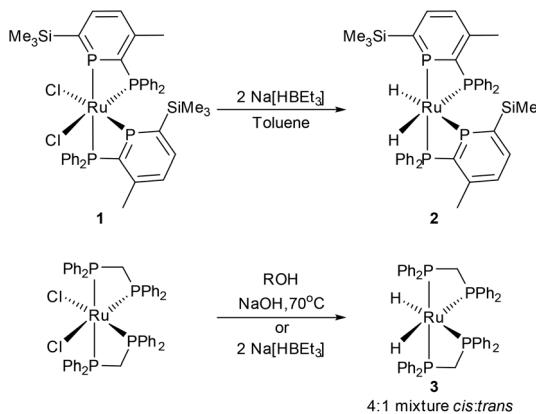
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Scheme 2 Synthesis of ruthenium dihydrides.

the production of an amine-formate adduct, thus demonstrating facile CO_2 conversion.⁴⁰ The development of phosphinines, the phosphorus analogue of pyridine, as effective ligands for homogeneous catalysis has grown over the last 25 years,^{41–43} and now includes applications such as Rh-catalysed hydroformylation⁴⁴ and hydrogenation,^{45,46} Au-catalysed cycloisomerisations,⁴⁷ Cr-catalysed ethylene oligomerisation⁴⁸ and the hydroboration of carbonyls.⁴⁹ The application of homogeneous metal-phosphinine catalysts to confront energy challenges has also been explored, including in water oxidation reactions⁵⁰ and the catalytic upgrading of alcohols to advanced biofuels.⁴⁶ Previous work in our group has demonstrated that Ru catalysts based on the bidentate chelating phosphinophosphinine ligand 2- PPh_2 -3-Me-6-SiMe₃-PC₅H₂ (PP') catalysed the room temperature transfer hydrogenation of acetophenone and the H-borrowing upgrading of alcohol fuels.^{46,51} Ruthenium hydrides are implicated in many catalytic reactions, yet the first Ru complex comprising of both a hydride and phosphinine ligand has only been described recently by us.⁵² Herein, we describe the first ruthenium phosphinine dihydride complex and compare its catalytic activity to that of classical diphosphine-supported complexes for AD reactions.

Ruthenium dihydride fragments supported by phosphine ligands are well known, and have proven to be successful catalysts for numerous reactions, as well as suitable precursors for photochemical C–H activation.^{53,54} $[\text{Ru}(\text{H})_2(\text{dppm})_2]$ exists as a mixture of *cis* and *trans* isomers⁵⁵ and can be synthesised from $[\text{Ru}(\text{Cl})_2(\text{dppm})_2]$ ⁵⁶ through reaction with primary or secondary alcohols and NaOH,⁵⁷ or by reaction with Na[BHET₃] (Scheme 2). Building on recent work describing a $[\text{RuCp}^*(\text{H})]$ fragment supported by a bis(phosphinine) ligand,⁵² the ruthenium dihydride *cis*- $[\text{Ru}(\text{H})_2(\text{PP}')_2]$ (2) was synthesised from the dichloro precursor *cis*- $[\text{Ru}(\text{Cl})_2(\text{PP}')_2]$ (1) by reaction with two equivalents of Na[BHET₃] (Scheme 2).[§]

[§] Analytical data for 2: ¹H-NMR (400 MHz, C₆D₆, 298 K): δ = 8.26 (m, 2H, $\text{CH}_{\text{arom.}}$), 7.78 (m, 2H, $\text{CH}_{\text{arom.}}$), 7.57 (ddd, 1H, $\text{CH}_{\text{arom.}}$), 7.48 (m, 3H, $\text{CH}_{\text{arom.}}$), 7.16 (m overlapping with C₆D₅H), 7.05–6.89 (m, 7H, $\text{CH}_{\text{arom.}}$), 6.87 (m, 3H, $\text{CH}_{\text{arom.}}$), 6.77 (m, 2H, $\text{CH}_{\text{arom.}}$), 6.37 (dd, 2H, $\text{CH}_{\text{arom.}}$), 1.64 (s, 3H, CH_3), 1.61 (s,

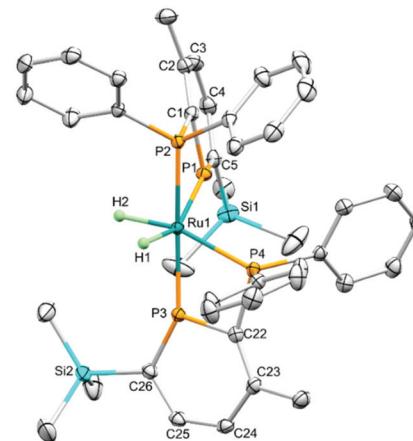


Fig. 1 Molecular structure of 2 (thermal ellipsoids at 50% probability). All H atoms except for the two metal hydrides have been removed for clarity. Selected bond distances (Å) and angles (°): Ru1–H1 1.60(3), Ru1–H2 1.57(3), Ru1–P1 2.2795(5), Ru1–P3 2.2634(5), Ru1–P2 2.3071(5), Ru1–P4 2.3889(5); H1–Ru1–H2 79(2), P1–Ru1–P2 70.37(2), P1–Ru1–P4 109.05(2), P2–Ru1–P3 (3) 175.26(3).

The formation of *cis*- $[\text{Ru}(\text{H})_2(\text{PP}')_2]$ (2) was evident by an immediate colour change of orange to bright red upon the addition of Na[BHET₃] to 1. ³¹P{¹H} NMR spectroscopy confirmed the presence of only four resonances, two at high chemical shift indicative of phosphinine groups, and two at lower chemical shift from the diphenylphosphino groups. Two doublet-of-doublet-of-doublets resonances were observed with a large *trans*-coupling (261 Hz), which has decreased compared to the *trans* ²J_{PP} coupling in 1 (425 Hz). The ¹H NMR spectrum displayed resonances for two inequivalent PP' ligands as well as two multiplet resonances at –6.55 and –7.04 ppm for the two Ru–H.[§]

Slow evaporation of a petroleum ether solution of 2 in a globox yielded crystals suitable for structural characterisation using X-ray diffraction.[¶] The crystal structure of 2, Fig. 1, shows Ru(1) in a slightly distorted octahedral geometry with two phosphinophosphinine and *cis*-dihydride ligands, which were located in the Fourier difference map and refined. The phosphinine donors are *cis*-disposed, due to their strong π -accepting character, and this explains why only one isomer of 2 was formed (as a racemic mixture). The bond lengths of the phosphinine phosphorus atoms P(1) and P(3) to Ru(1) (2.2795(5) and 2.2634(5) Å respectively) are shorter than the

3H, CH_3), 0.62 (s, 9H, SiMe₃), 0.27 (s, 9H, SiMe₃), –6.55 (m, 1H, H_{hydride}), –7.04 (m, 1H, H_{hydride}) ppm; ³¹P{¹H}-NMR (162 MHz, C₆D₆, 298 K): δ = 253.3 (ddd, ²J_{P₂–P₄} = 291 Hz, P₂), 250.4 (m, P₁), 31.6 (ddd, ²J_{P₁–P₂} = 291 Hz, P₄), 15.7 (m, P₃) ppm; HRMS (APCI/QTof) *m/z*: calcd for [C₄₂H₄₉P₄⁹⁶RuSi₂]⁺ 829.1400 [M – H]⁺, found 829.1404; calcd for [C₃₀H₄₀P₃RuSi₂]⁺ 651.0919 [M – HPPH₂]⁺, found 651.0930.

[¶] Crystal data for C₄₂H₅₀P₄RuSi₂ ($M = 835.95$ g mol^{–1}): monoclinic, space group P2₁/n (no. 14), $a = 14.5408(5)$ Å, $b = 10.5871(3)$ Å, $c = 27.8908(9)$ Å, $\beta = 104.1980$ (10)°, $V = 4162.5(2)$ Å³, $Z = 4$, $T = 100.0$ K, $\mu(\text{Cu}-\text{K}\alpha) = 5.263$ mm^{–1}, $D_{\text{calc}} = 1.334$ g cm^{–3}, 129 865 reflections measured (6.538° $\leq 2\theta \leq 156.18^{\circ}$), 8484 unique ($R_{\text{int}} = 0.0386$, $R_{\text{sigma}} = 0.0152$). The final R_1 was 0.0250 ($I > 2\sigma(I)$) and wR_2 was 0.0606. CCDC: 2083014.[‡]



distances from the diphenylphosphino phosphorus atoms P(2) and P(4) to Ru(1) (2.3071(5) and 2.3889(5) Å respectively). The angles between phosphorus atoms on the same ligand, *e.g.* P(1)–Ru(1)–P(2) (70.37(2)°), are smaller than that of phosphorus atoms on different ligands (*e.g.* P(1)–Ru(1)–P(4): 109.05(2)°), showing the distortion from octahedral geometry.

Despite the clean synthetic route, attempts to isolate **2** were problematic whenever **2** was dried under vacuum. Upon exposure to vacuum, the resulting $^{31}\text{P}\{\text{H}\}$ NMR spectra displayed many resonances of weak intensity instead of the anticipated product. Analysis by mass spectrometry (APCI) corroborated these results with only very low intensity signals for masses above 300 Da. This was indicative that drying under vacuum led to the decomposition of **2**. Isolation of **2** by evaporation of the solvent under a stream of nitrogen led to the successful isolation of **2** in modest yields (25 mg, 27%). The mass spectrum now displayed a mass envelope centred at 835 Da with the correct isotopic distribution and accurate mass for $[\text{C}_{42}\text{H}_{49}\text{P}_4\text{RuSi}_2]^+$, $[\text{M} - \text{H}]^+$.

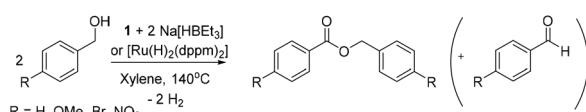
Complex **1** was used as a precatalyst for **2** in the acceptorless dehydrogenation of benzyl alcohols (Scheme 3) (Table 1).

Four benzyl alcohols with different electron donating and withdrawing substituents were screened to test the reactivity of **2**. These reactions were compared to the catalytic activity of $[\text{Ru}(\text{H})_2(\text{dppm})_2]$ (**3**). Base line reactions with no Ru catalyst gave no formation of benzyl benzoate, and when only Na[HBET₃] was added, there was only a small amount of benzaldehyde produced (0.5%). Using 1 mol% of **2**, a 28% yield of ester was evident after 45 hours at 140 °C (run 1), which is

higher than for **3** (19%, run 9). Doubling the catalyst concentration and increasing the reaction time led to better conversions, thereby increasing yields (run 3: 61% for **2**, run 11: 38% for **3** after 94 hours) up to 70% benzyl benzoate for **2**. The addition of base (NaO^tBu) did not increase yields. Substitution of the benzyl alcohol with a *para*-methoxy group led to significant production of the substituted benzaldehyde as the favoured product (30%, run 6). Electron withdrawing substituents inhibit the acceptorless dehydrogenation reaction (*para*-NO₂: 12%, run 8; *para*-Br: 11%, run 7), although the Br-substituted aldehyde by-product is also observed to a considerable extent (11%). In comparison $[\text{RuH}_2(\text{dppm})_2]$ produced similar yields and outcomes for substituted benzaldehydes.

Comparisons between different catalysts can be made for the coupling of benzyl alcohol. The mixture of $[\text{RuCl}_2(p\text{-cymene})(\text{iPr})]$ (2.5 mol%), KOH (10 mol%) and PCy₃ (4.5 mol%) at 163 °C for 18 h gave a yield of 31% benzyl benzoate; benzyl alcohols with *para*-OMe and Me groups led to lower yields.⁵⁸ A RuCl₂ complex with an aryl-tethered phosphine ligand in combination with **2** equiv. NaO^tBu gave benzaldehyde as the product at 110 °C (2 mol%, 36 h, 80% yield).⁵⁹ $[\text{RuH}_2(\text{PPh}_3)_4]$ (2 mol%) at 180 °C in refluxing mesitylene gave 60% benzyl benzoate.¹⁵ We note that the use of $[\text{RuCl}_2(\text{PPh}_3)_3]$ did not lead to substantial amounts of ester formation (2.4%) even with the addition of KO^tBu.⁶⁰ Yields were found to be similar to **2** after 120 h using an imidazolyl phosphine ruthenium dichloride complex with the addition of base (KO^tBu).⁶⁰ Morton and Cole-Hamilton achieved high rates of hydrogen production from aliphatic alcohols using $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$, albeit at 150 °C.⁶¹ Aldehydes were synthesised from primary alcohols in moderately high yields with ruthenium triazolylidene dichloride complexes.⁶² In our work, an electron donating OMe substituent produced mixtures of ester:aldehyde products (run 6, 1 : 6; run 13, 1.6 : 2) in a higher ratio of aldehyde compared to an Ir-phosphine pincer catalyst (3 : 1).²⁴

In summary, we have prepared *cis*- $[\text{Ru}(\text{H})_2(\text{PP}')_2]$, the first metal dihydride supported by phosphinophosphinine ligands.



Scheme 3 The Ru-catalysed acceptorless dehydrogenation of benzyl alcohols.

Table 1 Ru-catalysed acceptorless dehydrogenation of benzyl alcohols

Entry	Cat.	Substrate R =	Temp (°C)	Loading (mol%)	Time (h)	Yield (%) ester	Yield (%) aldehyde	TON (TOF/h ⁻¹)
1 ^a	2	H	140	1	45	28	1	29 (0.6)
2 ^a	2	H	140	2	45	35	1	18 (0.4)
3 ^a	2	H	140	2	94	61	<1	31 (0.3)
4 ^a	2	H	140	2	140	70	<1	35 (0.3)
5 ^a	2	H	140	5	45	38	<1	8 (0.2)
6 ^a	2	OMe	140	2	45	5	30	18 (0.4)
7 ^a	2	Br	140	2	45	11	11	11 (0.2)
8 ^a	2	NO ₂	140	2	45	12	2	7 (0.2)
9	3	H	140	1	45	19	<1	19 (0.4)
10	3	H	140	2	45	27	1	14 (0.3)
11	3	H	140	2	94	38	<1	19 (0.2)
12	3	H	140	2	140	64	<1	32 (0.2)
13	3	OMe	140	2	45	16	20	18 (0.4)
14	3	Br	140	2	45	7	9	8 (0.2)
15	3	NO ₂	140	2	45	10	5	8 (0.2)

^a 1 + 2 equivalents Na[HBET₃]. Yields: average of two runs, quantified using 1,3,5-trimethoxy benzene as an internal standard. TON = (2 × mmol ester + mmol aldehyde if $\geq 1\%$) / mmol cat.

When formed *in situ* from the dichloride complex and Na[BH₃Et₃], the catalysed acceptorless dehydrogenative coupling of benzyl alcohols to esters was observed. While *cis*-[Ru(H)₂(PP')₂] showed improved catalytic activity compared to [Ru(H)₂(dppm)₂], its broadly similar activity to conventional Ru complexes in promoting the AD of benzyl alcohol into benzyl benzoate implies typical supporting ligand behaviour as opposed to metal-ligand cooperative pathways.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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