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A Ruthenium cis-Dihydride with 2-Phosphinophosphinidine Ligands Catalyses the Acceptorless Dehydrogenation of Benzyl Alcohol†

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The first ruthenium dihydride complex featuring a phosphinidine ligand cis-[Ru(H)$_2$(2-PP$_2$H$_2$-3-Me-6-SiMe$_3$-PC$_6$H$_3$)$_2$] was synthesised exclusively as the cis-isomer. When formed in-situ from the reaction of cis-[Ru(Cl)$_2$(2-PP$_2$H$_2$-3-Me-6-SiMe$_3$-PC$_6$H$_3$)$_2$] with two equivalents of Na[BHEt$_3$], as demonstrated by $^{31}$P and $^1$H 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 H$_2$ that is generated is a clean alternative fuel burning to produce solely water vapour, or H$_2$ 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(OCCF$_3$)$_2$(CO)(PPh$_3$)$_2$] alongside an acid promoter,13 related ruthenium(II) trifluoroacetate diphosphine complexes,14 [Ru(H)$_2$(PPh$_3$)$_2$], at 180°C,15-16 and Shvo’s catalyst at 145°C for the conversion of PhCH$_2$OH 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 deaeromatised 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 systems23-25 involving both precious metals and first row26-38 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(diphenyl-phosphinomethane) (dpdm).30 For example, the pre-catalyst cis-[Ru(Cl)$_2$(dpdm)$_2$] achieved an initial TOF of 180,000 h$^{-1}$ for the reaction of CO$_2$ with hydrogen in an amine solution leading to the production of an amine-formate adduct, thus demonstrating facile CO$_2$ conversion.40

![Scheme 1. Acceptorless dehydrogenation reactions of alcohols.](image)

Scheme 1. Acceptorless dehydrogenation reactions of alcohols.

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hydroformylation and hydrogenation. Au-catalysed cycloisomerisations, Cr-catalysed ethylene oligomerisation and the hydroboration of carbynyls. The application of homogeneous metal-phosphinine catalysts to confront energy challenges has also been explored, including in water oxidation reactions and the catalytic upgrading of alcohols to advanced biofuels. Previous work in our group has demonstrated that Ru catalysts based on the bidentate chelating phosphinophosphinine ligand 2-PPh_2-3-Me-6-SiMe_3-PC_6H_{14} (PP') catalysed the room temperature transfer hydrogenation of acetonophene and the H-borrowing upgrading of alcohol fuels. 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. 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. [Ru(H)(dpmm)_2] exists as a mixture of cis and trans isomers and can be synthesised through reaction with primary or secondary alcohols and NaOH, or by reaction with Na[BHEt_3] (Scheme 2). Building on recent work describing a [RuCp*(H)] fragment supported by a bis(phosphine) ligand, the ruthenium dihydride cis-[Ru(H)(PP)_2] (2) was synthesised from the dichloro precursor cis-[Ru(Cl)(PP)_2] (1) by reaction with two equivalents of Na[BHMe_2] (Scheme 2).

Despite the clean synthetic route, attempts to isolate 2 were problematic whenever 2 was dried under vacuum. Upon exposure to vacuum, the resulting ^31P(^1H) 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 [C_42H_48P_2RuSi_2]^{+}, [M-H]^+.

Complex 1 was used as a precatalyst for 2 in the acceptorless dehydrogenation of benzyl alcohols (Scheme 3).
Four benzyl alcohols with different electron donating and withdrawing substituents were screened to test the reactivity of \( \text{2} \). These reactions were compared to the catalytic activity of \([\text{RuH}_2(p\text{-dpmm})]\) \( \text{3} \). Base line reactions with no Ru catalyst gave no formation of benzyl benzoate, and when only Na[BETs] was added, there was only a small amount of benzaldehyde produced (0.5 %). Using 1 mol% of \( \text{2} \), a 28% yield of ester was evident after 45 hours at 140°C (run 1), which is higher than for \( \text{3} \) (19%, run 9). Doubling the catalyst concentration and increasing the reaction time led to better conversions, thereby increasing yields (run 3: 61% for \( \text{2} \), run 11: 38% for \( \text{3} \) after 94 hours) up to 70% benzyl benzoate for \( \text{2} \). The addition of base (NaOMe) 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-NO\(_2\): 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 \([\text{RuH}_2(p\text{-dpmm})]\) 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 PCy\(_3\) (4.5 mol%) at 163°C for 18hrs gave a yield of 31% benzyl benzoate; benzyl alcohols with para-OMe and Me groups led to lower yields. A RuCl\(_2\) complex with an aryl-tethered phosphine ligand in combination with 2 equiv. NaOMe gave benzaldehyde as the product at 110°C (2 mol%, 36 h, 80% yield). [RuH\(_2\)(PPh\(_3\))] (2 mol%) at 180°C in refluxing mesitylene gave 60% benzyl benzoate. We observed that use of \([\text{RuCl}_2(P\text{Ph}_3)]\) did not lead to substantial amounts of ester formation (2.4%) even with the addition of KOBu. Yields were found to be similar to 2 after 120 h using an imidazolyl phosphine ruthenium dichloride complex with the addition of base (KO\(_2\)Bu). Morton and Cole-Hamilton achieved high rates of hydrogen production from aliphatic alcohols using [RuH\(_2\)(N\(_2\))(PPh\(_3\))]\(_3\), albeit at 150°C. Aldehydes were synthesised from primary alcohols in moderately high yields with ruthenium triazolylidene dichloride complexes. 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).

In summary, we have prepared cis-[Ru(H\(_2\))(P\(_2\)P\(_3\))]\(_2\), the first metal dihydride supported by phosphinophosphine ligands. When formed in-situ from the dichloride complex and Na[BETs], the catalysed acceptorless dehydrogenative coupling of benzyl alcohols to esters was observed. While cis-[Ru(H\(_2\))(P\(_2\)P\(_3\))] showed improved catalytic activity compared to [Ru(H\(_2\))(pdpmm)]\(_2\), 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.

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**Conflicts of interest**

There are no conflicts to declare.

**Notes and references**
\[ \text{‡ Analytical data for 2:} \ \text{^1}H\text{-NMR (400 MHz, CD}_2\text{D}_2):} \ \delta = 8.26 \ (m, 2H, CH}_2\text{OCH}_3), 7.78 (m, 2H, CH}_2\text{OCH}_3), 7.57 (dd, 1H, CH}_2\text{OCH}_3), 7.48 \ (m, 3H, CH}_2\text{OCH}_3), 7.16 \ (m overlapping with C}_2\text{D}_2\text{H):} 7.05-6.89 \ (m, 7H, CH}_2\text{OCH}_3), 6.87 \ (m, 3H, CH}_2\text{OCH}_3), 6.77 \ (m, 2H, CH}_2\text{OCH}_3), 6.37 \ (dd, 2H, CH}_2\text{OCH}_3), 1.64 \ (3s, 3H, CH}_3), 1.61 \ (1s, 3H, CH}_3), 0.62 \ (5s, 9H, SiMe}_3), 0.27 \ (2s, 9H, SiMe}_3), -6.55 \ (1H, H}_\text{endo}), -7.04 \ (1H, H}_\text{exo})); \ \text{ppm:} \ \text{P}^{\text{31}}\text{(H)-NMR (162 MHz, CD}_2\text{D}_2):} \ \delta = 253.3 \ (ddd, 2J_{P2-P4} = 291 \text{ Hz,} P2, P4), 250.4 \ (m, P4), 31.6 \ (dd, 2J_{P2-P4} = 291 \text{ Hz,} P4), 15.7 \ (m, P3) \ \text{ppm; HRMS (APCI/TOF m/z:} \ \text{for [C}_2\text{H}_6\text{O}_4\text{P}_4\text{Ru}_2\text{Si]}^+ 829.1400 \ [M-H]^+), \ \text{found 829.1404; for [C}_2\text{H}_6\text{O}_4\text{P}_4\text{Ru}_2\text{Si]}^+ 651.0919 \ [M – HPP}_3]^+), \ \text{found 651.0930.} \ \text{§ Crystal Data for [C}_2\text{H}_6\text{O}_4\text{P}_4\text{Ru}_2\text{Si]}: \ M = 835.95 \ \text{g/mol;} \ \text{monoclinic, space group P2}_1/n \ (no. 14), a = 14.5408(5) \ \text{Å,} b = 10.5871(3) \ \text{Å,} c = 27.8900(9) \ \text{Å,} \ \theta = 104.1980(10)^\circ, V = 4162.52(2) \ \text{Å}^3, z = 4, T = 100.0 \ \text{K,} \mu (\text{Cu-K}α) = 5.263 \ \text{mm}^{-1}, D_{\text{calc}} = 1.334 \ \text{g/cm}^3, 129865 \ \text{reflections measured (6.538} \leq 2θ \leq 156.18^\circ), 8484 unique (R_{int} = 0.0386, R_{free} = 0.0152). \ \text{The final R}_1 = 0.0250 \ (I > 2σ(I)) \ \text{and wR}_2 = 0.0606. \ \text{CCDC:} 2803014. \]
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