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A ruthenium(II) bis(phosphinophosphinine) complex as a precatalyst for transfer-hydrogenation and hydrogen-borrowing reactions†

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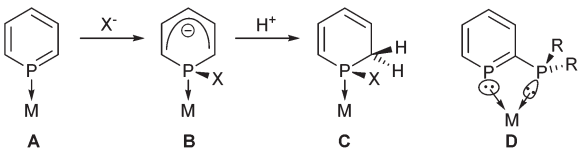
The 2-phosphinophosphinine 2-PPh_2-3-Me-6-$SiMe_3$-PC_5H_2 (2) has been prepared and was shown to act as a κ^2-chelating ligand in *cis*-[$RuCl_2$(2)$_2$] (4). Complex 4 was a competent precatalyst for the room temperature transfer hydrogenation of acetophenone (0.1 mol% 4 and 0.5 mol% KO^tBu) and the conversion of methanol/ethanol mixtures to the advanced biofuel isobutanol in 50% yield and 96% selectivity.

Phosphinines (the P-analogue of pyridine) have developed into useful ligands in coordination chemistry[1] and catalysis.[2] The LUMO of phosphinine (**A**) contains significant phosphorus p-character that leads to π-accepting behaviour, but can also lead to nucleophiles attacking the electrophilic P atom,[1b,3] followed by protonation (Scheme 1).[3b,4]

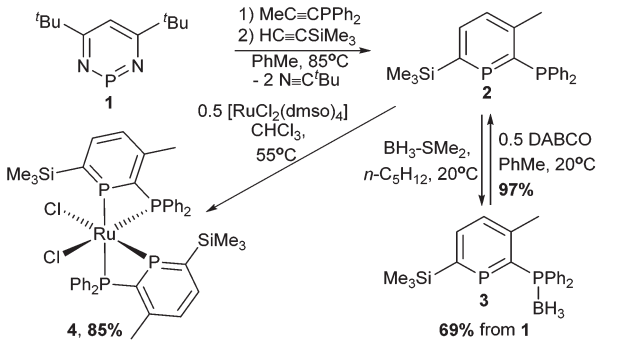
Conventionally, the electrophilicity of phosphinines has been viewed as problematic in catalysis,[5] however, the heterocyclic species **B** and **C** have been shown to be useful ligands in their own right.[1a,5,6] This electrophilic reactivity could therefore be used as part of a ligand activation strategy to produce new coordination complexes or turn precatalysts into catalysts.[7] Metal–ligand cooperation[8] and bifunctional catalysis[9] are both important topics in catalysis that have only emerged recently.

Donor-substituted phosphinines[10] are useful ligands because they combine the unique properties of phosphinines with more conventional donors, such as pyridine.[11] However, there are only a handful of methods for introducing phosphine substituents.[12] For example, bromophosphinines were shown to undergo Pd-catalysed coupling to produce 2-phosphinophosphinines.[13] In 1996, Mathey, Le Floch and co-workers demonstrated that diazaphosphinine **1** (Scheme 2) reacts in consecutive steps with alkynes to give 2,3,5,6-tetrasubstituted phosphinines, including 2-phosphinophosphinines.[14] However, reports of phosphinophosphinines in catalysis are limited to the use of a wide bite-angle phosphinophosphinine in the regioselective hydroformylation of styrene,[12b,15] and a Rh-phosphitophosphinine complex used in asymmetric hydrogenation catalysis.[16]

Transfer hydrogenation holds great potential in chemical synthesis because it replaces hazardous reducing agents, such as hydrogen gas or metal hydrides, with more convenient chemical sources of hydrogen, commonly isopropanol or



Scheme 1 Reactivity of coordinated phosphinines (**A**–**C**), and a 2-phosphinophosphinine (**D**).



Scheme 2 Synthesis of 2-phosphinophosphinine **2** and coordination to Ru.

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formic acid/formate.[17] Related to this are hydrogen-borrowing processes that involve the oxidation of a saturated substrate by transfer of an equivalent of dihydrogen to a metal centre, thereby facilitating new reactivity, before the borrowed hydrogen is then returned.[18] These fields have typically been dominated by Ru and Ir catalysts.[17,18] Recently there has been renewed interest in the Guerbet reaction,[19] a borrowed hydrogen process in which an alcohol is dehydrogenated to an aldehyde and then undergoes aldol condensation before rehydrogenation of the product to a longer chain alcohol.[20] Wass and co-workers reported that a family of Ru complexes with diphosphine[21] or aminophosphine[22] supporting ligands could selectively convert ethanol to *n*-butanol, or ethanol/methanol to isobutanol,[23] *via* the Guerbet reaction. Of the catalysts tested, *trans*-[$RuCl_2$(dppm)$_2$] (dppm = 1,1-bis(diphenylphosphino) methane) – containing a small bite-angle diphosphine ligand – proved to be the most active and stable,[21] whereas wider bite angle ligands were less active. We became interested in the greater s-character of the formally sp^2-hybridised P lone pair of phosphinine (estimated as *ca.* 61% for PC_5H_5)[1a] compared to conventional phosphines because we reasoned that the reduced directional preference would lead to less strained 4-membered chelate rings (**D**). Additionally, the ligand non-innocence of phosphinines has not been fully explored in catalysis, so we set out to synthesise a suitable chelating 2-phosphinophosphinine precatalyst and then screen this complex for catalytic reactivity in transfer hydrogenation and hydrogen borrowing reactions. Ligated $RuCl_2$ complexes are typical precatalysts for these reactions, and they are converted into the active catalysts by reaction with alkoxides.[24] The exact catalytic mechanisms are still under examination,[25] but are believed to involve metal hydrides.[24,26]

Using the methodology of Le Floch and Mathey,[14] the 2-phosphinophosphinine **2** was synthesised by sequential reaction of **1** with diphenylprop-1-ynylphosphine[27] and trimethylsilylacetylene in toluene at 85 °C over 2 days (Scheme 2). To facilitate product work-up, the borane adduct **3** was generated immediately after extraction of **2** from the crude reaction mixture by reaction with Me_2S–BH_3 at room temperature, and **3** precipitated as a colourless solid in good yield (69% from **1**). **3** was fully characterised by elemental analysis, single crystal X-ray diffraction, mass spectrometry and multinuclear NMR spectroscopy (see ESI†).

Deprotection of **3** by reaction with 0.5 equivalents of DABCO[28] (1,4-diazabicyclo[2.2.2]octane) at room temperature followed by removal of the insoluble DABCO·2BH_3 by filtration gave the parent phosphinophosphinine **2** as a pure pale-yellow solid. **2** is stable to ROH (R = Me, Et, ^{i}Pr) as well as atmospheric oxygen and moisture, greatly facilitating storage and handling, and batches of up to 3 g have been prepared from **1** in 5 days. $^{31}P\{^1H\}$ NMR spectroscopy showed a characteristic resonance at high frequency for the phosphinine P atom located in the aromatic ring (δ 249.8 ppm) coupled to the phosphine P at lower chemical shift (−7.5 ppm, $^2J_{PP}$ 31.6 Hz). These values are similar to the related silyl-substituted phosphinine 2,3-(PPh_2)$_2$-6-$SiMe_3$-PC_5H_2 (δ: 256 and −10 ppm).[14b] Complete characterisation was achieved using multinuclear NMR spectroscopy, elemental analysis and mass spectrometry. Single crystal X-ray diffraction experiments confirmed the molecular structure of **2** (Fig. 1A and Table S2†). Although the X-ray crystal structures of approximately 30 uncoordinated phosphinines are known,[29] compound **2** represents the first structural determination of an unfunctionalised 2-phosphinophosphinine. The P–C bond lengths in the aromatic ring (*ca.* 1.75 Å) are intermediate between P–C single (*ca.* 1.83 Å) and double (*ca.* 1.66 Å) bonds.[1b] The C–C bond lengths are similar to the C–C bond length in benzene (1.40 Å), although C1–C2 is slightly longer (1.423(4) Å). One P–Ph bond is located in the plane of the phosphinine ring and the other is perpendicular. This has the effect of orienting the phosphine lone pair away from any potential overlap with the phosphinine ring, and the Ph_2P–C bond length resembles a standard single bond (1.847(3) Å).

Coordination to Ru was accomplished by reacting two equivalents of **2** with [$RuCl_2$(dmso)$_4$] at 55 °C in $CHCl_3$ for 5 hours to give *cis*-[$RuCl_2$(**2**)$_2$] (**4**) as a bright orange solid. Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy showed consumption of the two doublets observed for **2** and the concomitant appearance of four multiplets, two at high frequency and two around 0 ppm that integrated in a 1 : 1 : 1 : 1 ratio. Large *trans*-couplings ($^2J_{PP}$ 425 Hz) were observed for one phosphinine and one phosphine P atom. The presence of these *trans*-couplings suggested the selective formation of the C_1 *cis*-isomeric structure for **4** (as a racemic mixture of its enantiomers), which was confirmed by single crystal X-ray diffraction experiments (Fig. 1B and Table S2†).

The solid-state structure of **4** showed the first crystallographic evidence of κ^2 coordination of a 2-phosphinophosphinine to a transition metal. The molecular structure of **4** showed a distorted O_h Ru centre with *cis*-Cl ligands and two

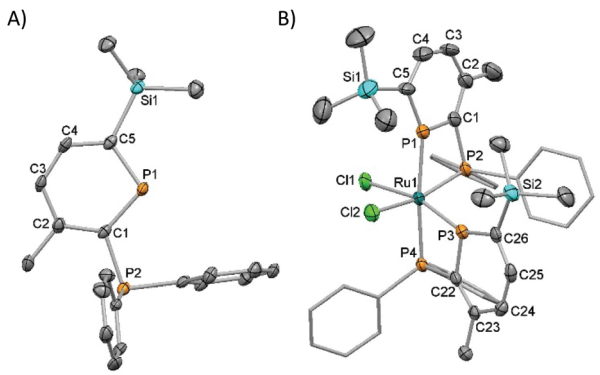


Fig. 1 Thermal ellipsoid plots (50%) of the molecular structures of **2** (A) and **4** (B, Ph rings in **4** are displayed without thermal ellipsoids for clarity). Selected bond distances (Å) and angles (°) for **2**: P(1)–C(1) 1.754 (3), C(1)–C(2) 1.423(4), C(2)–C(3) 1.404(4), C(3)–C(4) 1.393(4), C(4)–C(5) 1.396(4), C(5)–P(1) 1.749(3), C(1)–P(2) 1.847(3), C(1)–P(1)–C(5) 103.6(1), P(1)–C(1)–P(2) 119.9(1); for **4**: P(1)–Ru(1) 2.310(2), P(2)–Ru(1) 2.342(2), P(3)–Ru(1) 2.241(2), P(4)–Ru(1) 2.369(2), Ru(1)–Cl(1) 2.430(2), Ru(1)–Cl(2) 2.477(2), P(1)–Ru(1)–P(2) 69.89(6), P(3)–Ru(1)–P(4) 70.32(5).

inequivalent, bidentate 2-phosphinophosphinine ligands. The shortest Ru–P bond (P(3)–Ru(1) 2.241(2) Å) is to the phosphinine *trans* to a Cl, the longest (P(4)–Ru(1) 2.369(2) Å) to the phosphine *trans* to a phosphinine. The Ru–Cl bond lengths are similar, with the Ru–Cl bond length to Cl(1) *trans* to a phosphinine donor slightly shorter. The reasons behind the selective formation of one isomer are not completely clear, but the C_1 isomer does avoid either both phosphinines, or both phosphines, being *trans* to each other. Whilst a handful of bridging bimetallic complexes of 2-phosphinophosphinines are known (in reactions with CuI, $[Ni(cod)_2]$/CO, $Mn_2(CO)_{10}$ and $[M_2Cp_2(CO)_4]$ (M = Fe, Mo)),[30] to the best of our knowledge, there is only one brief mention of mono-metallic κ^2 complexes (to Gp 6 carbonyls).[12c] The bite angles of the two bidentate ligands in **4** are 69.89(6)° and 70.32(5)°, which are smaller than in *cis*-$[RuCl_2(dppm)_2]$ (72.1(3)°)[31] and *trans*-$[RuCl_2(vdpp)_2]$ (73.12(2)°, vdpp = 1,1-bis(diphenylphosphino)ethene),[32] but similar to *cis*-$[RuCl_2(Ph_2PCH_2phospholyl)_2]$ (71.12(5) and 70.53 (4)°).[33] **4** was further characterised by elemental analysis and mass spectrometry. Phosphinines with small *ortho*-substituents were previously shown to bind to Ru in an η^1 fashion in *trans*-$[RuCl_2(PC_5H_5)_4]$[34] or $[Ru(\eta^5\text{-}C_5Me_5)(2\text{-Br-}4,5\text{-}Me_2\text{-}PC_5H_2)Cl]$,[35] but η^6 coordination was favoured in $[Ru(\eta^5\text{-}C_5Me_5)(2,6\text{-}(SiMe_3)_2\text{-}PC_5H_3)][BF_4]$ with larger *ortho*-substituents.[35]

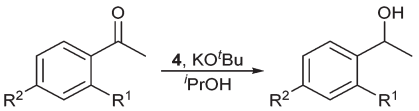
Complex **4** was subsequently tested as a precatalyst for the transfer-hydrogenation of substituted acetophenones. All of the substrates were tested using 0.1 mol% **4** and 0.5 mol% KO^{t}Bu in isopropanol at room temperature (Table 1). Good conversion to 1-phenylethanol was observed within one hour at room temperature (94%, run 1), and this was also observed for *para*-Br and -F acetophenone (97 and 96% respectively, runs 2 and 3). Electron-donating groups required heating and substrates with *para*-Me and *ortho*-OMe substitution went to excellent conversion at the boiling point of isopropanol (runs 5 and 7). Substrates with *para*-OMe (runs 8 and 9) and -NO_2 substituents (runs 10 and 11) only proceeded to moderate conversion even at 82 °C.‡

These results show that **4** is an excellent precatalyst for transfer hydrogenation of acetophenones at room temperature. In comparison, 0.1 mol% $[RuCl_2(PPh_3)_3]$ achieved only a 75% conversion of acetophenone after 6 hours at 82 °C.[36] Other Ru complexes with phosphorus ligands (including tripodal phosphines and a PCP pincer ligand) also required heating to achieve good conversion.§ $[Ru(\eta^6\text{-}p\text{-cymene})\{1\text{-Bu-}2\text{-}P(S)Ph_2\text{-}3\text{-Me-}5,6\text{-}Ph_2\text{-}PC_5H\}Cl]$, a Ru complex of a phosphacyclohexadienyl anion bearing a sulfur donor, was also shown to perform poorly as a catalyst requiring 2.5 days at 80 °C to go to completion.[6] A catalyst with a higher activity (full conversion after 1 minute at room temperature) has been demonstrated with a Ru complex bearing NH functionality that undergoes ligand-activation with base,[37] and a Ru pyridyl-phosphole complex has shown full conversion at extremely low loadings (5×10^{-6} mol%) at 90 °C.[38] §

Activation of the precatalyst with KO^{t}Bu could affect the phosphinine moieties (leading to **B** and **C**) as well as substituting the Cl ligands. This was demonstrated by $^{31}P\{^1H\}$ NMR spectroscopy that revealed loss of the high frequency phosphinine resonances in **4** and formation of a major species with resonances at 70 and 20 ppm upon reaction with KO^{t}Bu in ^{i}PrOH at 20 °C, along with a number of other resonances. Analysis of these reaction mixtures re-dissolved in acetone-d_6 also demonstrated that many species were present with their chemical shifts indicating complete transformation of the phosphinine moieties. Mass spectrometry experiments similarly revealed multiple new species in the ≈ m/z 700–1200 range.† Clearly, there are many processes involved in the activation of the precatalyst.

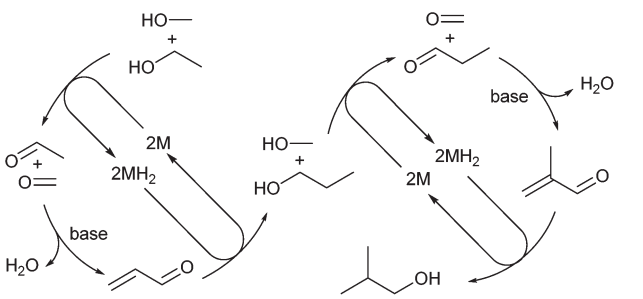
Complex **4** was tested for activity in the co-condensation of methanol and ethanol (Scheme 3).[19a,23] In this process methanol and ethanol are dehydrogenated to formaldehyde and acetaldehyde, which undergo aldol coupling to yield, after rehydrogenation, *n*-propanol. A further dehydrogenation, aldol coupling, re-hydrogenation cycle with a second equivalent of methanol yields isobutanol. Using standard conditions (see ESI†) **4** was found to produce isobutanol in 38% yield with good selectivity (88%) after 2 h in the liquid fraction.¶ In com-

Table 1 Transfer hydrogenation of substituted acetophenones using complex **4**



Run	R^1	R^2	Temperature	Conv.[a] (%)
1	H	H	20 °C	94%
2	H	Br	20 °C	97%
3	H	F	20 °C	96%
4	H	Me	20 °C	87%[c]
5			82 °C	98%
6	OMe	H	20 °C	5%[c]
7			82 °C	>99%
8	H	OMe	20 °C	48%[c]
9			82 °C	79%[c]
10	H	NO_2	20 °C	5%[b]
11			82 °C	72%[c]

Conditions: **4** (0.1 mol%), KO^{t}Bu (0.5 mol%), ^{i}PrOH, (0.4 M [substrate]), 1 h. [a] Conversion determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene internal standard, average of two runs. [b] 24 h run, low conversion due to insolubility of substrate. [c] No increase in conversion after 2 h.



Scheme 3 Co-condensation of MeOH and EtOH *via* a hydrogen borrowing mechanism.

parison, the previously reported catalyst, *trans*-[$RuCl_2(dppm)_2$] gave 65% isobutanol (98% selectivity).[23] The reduction in selectivity is due to a larger proportion of the intermediate *n*-propanol being formed (5% yield). Extending the reaction time to 20 h led to an increase in both isobutanol yield (50%) and selectivity (96%), similar to results obtained using the phosphinoamine based catalyst *trans*-[$RuCl_2(Ph_2P(CH_2)_2NH_2)_2$] (51% yield, 90% selectivity after 20 h).[23]

In conclusion, a bidentate 2-phosphinophosphinine ligand has been prepared along with the *cis*-ruthenium dichloride complex **4**, which contains two κ^2-chelating phosphinophosphinine ligands. **4** was shown to act as a precatalyst for the transfer hydrogenation of acetophenone at room temperature to 94% conversion in one hour upon activation with KO^{t}Bu. Substrates with electron withdrawing groups (*para*-Br, *para*-F) also proceeded to good conversion at room temperature, and substrates with electron donating groups (*para*-Me and *ortho*/*para*-OMe) reacted at higher temperatures (82 °C). Complex **4** was also an effective precatalyst for the upgrading of MeOH/EtOH mixtures to isobutanol in 50% yield and 96% selectivity over 20 hours. This demonstrates the first use of 2-phosphinophosphinines in catalysis.

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Notes and references

‡Throughout the catalytic runs, clear, homogeneous, orange solutions were observed with one exception; *para*-nitro acetophenone formed a dark brown solution and the substrate was poorly soluble in isopropanol. Nanoparticles have been implicated in the transfer hydrogenation catalysis of [$RuCl_2(PPh_3)_3$], although particularly under boiling conditions.[25b]

§See ESI† for a comparison of selected literature systems used in transfer hydrogenation of acetophenone.

¶As with previous reports, both solid and gaseous products are also formed during catalysis. ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy showed that the solid contains sodium formate. During the reactions a pressure build up is observed, for example, during the 2 h experiment the internal reactor pressure reaches approximately 32 bar. After cooling, approximately 12 bar pressure remains. This gas is presumably hydrogen formed as a by-product of formate synthesis.

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