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Homogeneous Catalysis

On the Functional Group Tolerance of Ester Hydrogenation and Polyester Depolymerisation Catalysed by Ruthenium Complexes of Tridentate Aminophosphine Ligands

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Abstract: The synthesis of a range of phosphine-diamine, phosphine-amino-alcohol, and phosphine-amino-amide ligands and their ruthenium(II) complexes are reported. Five of these were characterised by X-ray crystallography. The activities of this collection of catalysts were initially compared for the hydrogenation of two model ester hydrogenations. Catalyst turnover frequencies up to 2400 h^{-1} were observed at 85 °C. However, turnover is slow at near ambient temperatures. By using a phosphine-diamine Ru^{II} complex, identified as the most active catalyst, a range of aromatic esters were reduced in high yield. The hydrogenation of alkene-, diene-, and alkyne-functionalised esters was also studied. Substrates with a remote, but reactive terminal alkene substituent could be reduced chemoselectively in the presence of 4-dimethylaminopyridine (DMAP) co-catalyst. The chemoselective reduction of the ester function in conjugated dienoate ethyl sorbate could deliver (2*E*,4*E*)-hexa-2,4-dien-1-ol, a precursor to leaf alcohol. The monounsaturated alcohol (*E*)-hex-4-en-1-ol was produced with reasonable selectivity, but complete chemoselectivity of C=O over the diene is elusive. High chemoselectivity for the reduction of an ester over an alkyne group was observed in the hydrogenation of an alkynoate for the first time. The catalysts were also active in the depolymerisation reduction of samples of waste poly(ethylene terephthalate) (PET) to produce benzene dimethanol. These depolymerisations were found to be poisoned by the ethylene glycol side product, although good yields could still be achieved.

Introduction

The catalytic reduction of esters to alcohols by using molecular hydrogen can be considered an attractive method relative to the use of stoichiometric reducing agents. Improved atom economy, reduced cost, and safer, easier product isolation are key advantages. Heterogeneous metal surface catalysts can accomplish this task rather well, albeit generally at high pressures.[1] Moreover, many useful functional groups such as alkene, halide, ketone, benzyl, and sometimes even phenyl groups are hydrogenated under typical ester hydrogenation conditions. Homogeneous catalytic ester hydrogenation has been put forward as a potentially valuable reaction that could be chemoselective and operate under mild conditions.[2,4] For a long time, and until quite recently, this was just a possibility,[4] but in recent years ester hydrogenation has come of age.[5] A variety of catalysts have now given encouraging results. Our interest in this reaction started around ten years ago with a study of the chiral phosphine-diamine catalyst **1** (Figure 1). However, we observed fairly moderate results when using **1** for ester hydrogenation with procedures that we had optimised for enantioselective ketone reduction.[6a] More recently, after noticing the tendency for more modern ester hydrogenation catalysts to need rather large base/catalysts ratios, we communicated the use of achiral catalyst **4** (Figure 1) that can reduce aromatic esters at near ambient temperatures provided that base/catalyst ratios of 30 to 50 are employed.[7] Here, we give a full account of this work, including comparisons with other related ligand systems. We also now address the unresolved question of the relative rates of reduction of esters, alkene, diene, and alkyne functional groups, and study the depolymerisation of a polyester.

Results and Discussion

The chiral ketone hydrogenation catalysts **1**, **2** and achiral **3** were prepared as described before;[6] an optimised synthesis of **2** and **4** at multigram scale is archived in the Experimental Section (the Supporting Information). The synthesis of new Ru complexes **5**–**7** is also described. The crystal structure of **2** has now been solved and is shown in Figure 2. Although the formula has always been clear from the NMR spectrum, MS, and microanalytical data, this structure confirms several aspects that were previously unknown. The structure shows the meridional coordination of the *P,N,*O ligand. The DMSO ligand is co-

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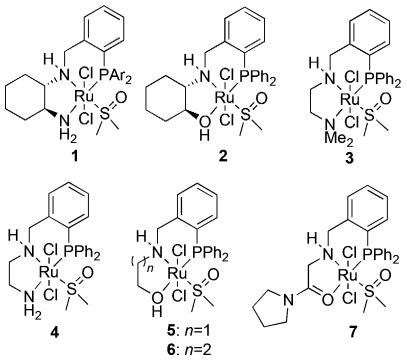


Figure 1. Ruthenium complexes of phosphine-diamine, phosphine-amino-alcohol and phosphine-amino-amide ligands used in this study.

ordinating through sulfur, rather than oxygen, and the chlorides adopt mutually *trans* orientations. The phosphine amino-alcohol is in a neutral coordination mode with the nitrogen atom becoming chiral at N on coordination to Ru. In many ways this structure is similar to the structure of **1** that we previously reported.[6a]

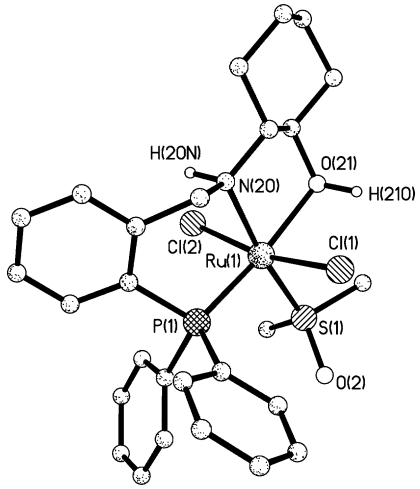


Figure 2. X-ray structure of complex **2**. Two acetonitrile molecules and hydrogen atoms (except N*H* and O*H*) are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ru–P(1) 2.256(1), Ru–N(20) 2.151(5), Ru–O(21) 2.205(3); O(21)-Ru-P(1) 171.31(9), N(20)-Ru-P(1) 92.3(1), N(20)-Ru-O(21) 79.2(1).

The synthesis of the achiral ethylene-diamine-derived catalyst **4** is described in the Supporting Information and works well providing the optimised procedure is followed. Catalyst **4** was characterised by using X-ray crystallography (Figure 3). This complex has a rather similar structure to the phosphine amino-alcohol complex **2**; a similar meridional neutral coordination mode, sulfur-bound DMSO ligand, and *trans* chloride ligands are all observed. Ru^{II} complex **7** and its ligand precursor, are, to the best of our knowledge, new species and also can be synthesised conveniently at multigram scale (the Supporting Information).

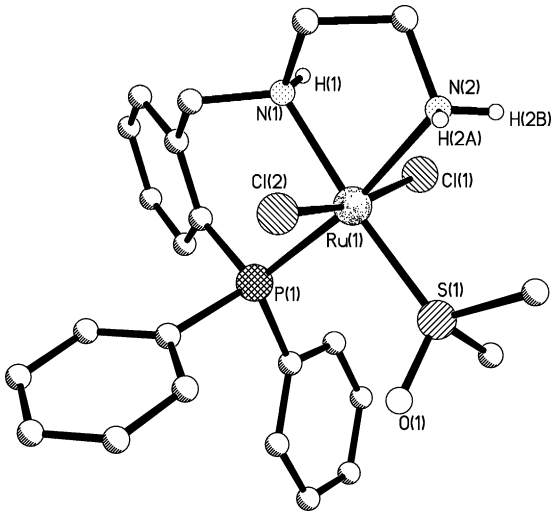


Figure 3. X-ray structure of complex **4**. One molecule of acetonitrile and hydrogen atoms (except N*H* and NH_2) are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ru–P(1) 2.2806(7), Ru–N(1) 2.130(2), Ru–N(2) 2.164(2); N(2)-Ru-P(1) 170.84(6), N(1)-Ru-P(1) 91.10(5), N(1)-Ru-N(2) 79.89(7).

This ligand was explored because it has a very low steric demand around the amide oxygen, but this terminus also cannot be readily deprotonated or form hydrogen bonds under the reaction conditions. The Ru^{II} complex was also structurally characterised (Figure 4). As expected, this is a PNO donor ligand that prefers a meridional coordination. The relative orientation and coordination mode of the chloride and DMSO ligands is as discussed above. The nitrogen of the amide is, as expected, planar as clearly indicated by the short Csp^2–Nsp^2 bond length of 1.326(7) Å and the N-C-O angle (120.6(4)°). With this series of complexes and the previously published structure of **1**,[6a] it can be seen that the longer Ru–P bond lengths across the series correspond to PNN complexes **1** and **4**, 2.2912 (13) and 2.2806(7) Å, respectively. The PN-alcohol complexes **2** and **6** and PN-amido complex **7** all have shorter Ru–P bonds because the amide and alcohol are weaker *trans* labilising ligands. In the PN-amido complex **7**, binding through a sp^2 oxygen, the Ru–O bond is shorter, 2.156(3) Å, in comparison with those of complexes **2** and **6**, 2.205(3) and 2.188(3) Å, respectively. Geometry around the metal centre exerts an important effect in catalysis.

The PNN and PNO ligands used in complexes **1**–**5** and **7** are chelating the Ru centre through a P atom and the N or the O atoms, thus forming one six-membered and one five-membered chelate ring. Complex **6** (Figure 5), with two six-membered chelate rings, was prepared to study the effect of increasing the size of the chelate ring of the pre-catalyst in the ester hydrogenation reaction. Ru complex **6** and its ligand precursor are, to the best of our knowledge, new species (full details in the Supporting Information). The N-Ru-O angle in complex **6** was, as expected, the largest (87.2(1)°), followed by PNO complex **2** (79.2(1)°) and amido complex **7** (77.2(1)°). The N-Ru-N angle in PNN complex **4** (79.89(7)°) was very similar to the N-Ru-O angle in **2** (79.2(1)°).

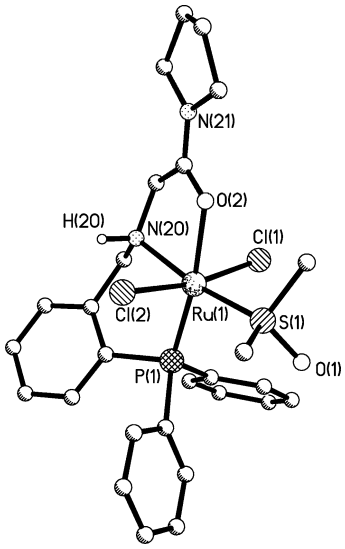


Figure 4. X-ray structure of complex **7**. Hydrogen atoms (except N*H*) are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ru–P(1) 2.254(1), Ru–N(20) 2.152(4), Ru–O(2) 2.156(3); O(2)-Ru-P(1) 170.66(9), N(20)-Ru-P(1) 93.4(1), N(20)-Ru-O(2) 77.2(1).

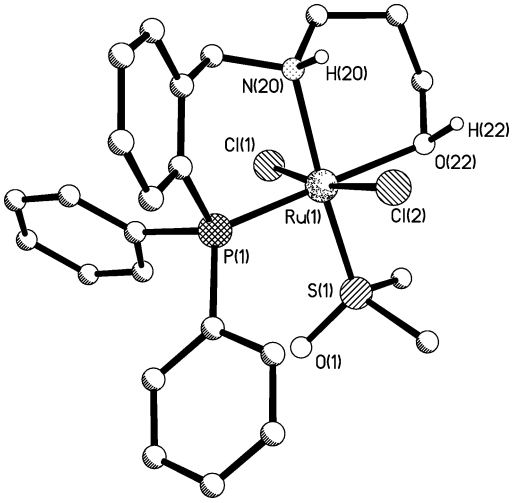
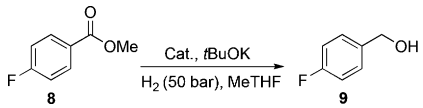


Figure 5. X-ray structure of complex **6**. Hydrogen atoms (except N*H* and O*H*) are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ru–P(1) 2.254(1), Ru–N(20) 2.200(4), Ru–O(22) 2.188(3); O(22)-Ru-P(1) 175.5(1), N(20)-Ru-P(1) 92.1(1), N(20)-Ru-O(22) 87.2(1).

With a range of pre-catalysts in hand, it was felt that some useful information on catalyst design could be obtained from testing this family in the catalytic hydrogenation of esters. Our initial screening methodology used a simple aromatic ester, *para*-fluorobenzoic acid methyl ester **8** as a substrate (Table 1). To compare the performance of catalysts under similar conditions, several small reactor vials were placed inside larger pressure vessels. It can be seen that each of these stirs to the same extent and will be under the same pressure and heat. These conditions are suited to comparing a single variable, keeping other conditions constant, and have been used in many other studies in our group. These are not necessarily optimised conditions in terms of turnover or minimising pressures; gas mixing relative to a large vessel with direct stirring will not be as effective, hence the use of 50 bar pressure to minimise mass transport problems. Catalysts **1**–**7** were initially examined at 65 °C for just 2 h using base/catalyst ratios of 50:1 (Table 1, entries 1–7).

Table 1. Hydrogenation of *para*-fluorobenzoic acid methyl ester using $[RuCl_2(P\hat{}N\hat{}X)(dmso)]$ complexes as pre-catalysts.



8 **9**

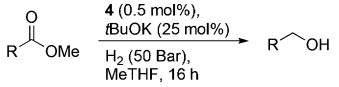
Entry[a]	Cat.	Load [mol%]	*t*BuOK/ cat.	*t* [h]	*T* [°C]	Product[b] [%]
1	**1**	0.5	40:1	2	65	37
2	**2**	0.5	40:1	2	65	97
3	**3**	0.5	50:1	16	100	43
4	**4**	0.5	40:1	2	65	94
5	**5**	0.5	40:1	2	65	84
6	**6**	0.5	40:1	2	65	25
7	**7**	0.5	40:1	2	65	23
8	**4**	0.5	50:1	2	100	97
9	**4**	0.5	30:1	16	50	93
10	**4**	0.2	50:1	16	50	>99
11[c]	**4**	0.5	50:1	16	50	0
12	**4**	0.5	50:1	64	30	69
13	**4**	0.5	50:1	100	30	>99

[a] Unless otherwise stated, the reactions were carried out by using 0.5 mol% $[RuCl_2(P\hat{}N\hat{}X)(dmso)]$, *t*BuOK as base (50:1, base/catalyst) at 100 °C at an initial pressure of 50 bar with 0.4 mmol of *para*-fluorobenzoic acid methyl ester in Me-THF (3 mL). [b] Conversion determined by ^{19}F NMR spectroscopy. [c] Use of KOH or MeONa as base gives no conversion.

Catalyst **3** was tested at 100 °C initially and not tested further due to its low activity (Table 1, entry 3). The new catalysts **5**–**7** were then benchmarked in the ester hydrogenation reaction (Table 1, entries 5–7). PNO Complex **7** proved to be a poor catalyst under the reaction conditions employed (Table 1, entry 7), but the achiral PNO complex **5**, structurally similar to complex **4**, achieved good levels of activity (entry 5). Increasing the size of the chelate ring as in complex **6** proved to be detrimental to the activity of the complex in the ester hydrogenation reaction (Table 1, entry 6 vs. 5). This type of reactivity has been observed in transfer hydrogenation.[8] Complexes **2** and **4** showed the highest level of activity, achieving near full conversion within 2 h. Reaction conditions were next studied using relatively cheap achiral catalyst **4** (Table 1, entries 8–13). Catalyst loadings down to 0.2 mol% (Table 1, entry 10) and base/catalyst ratios down to 30:1 (Table 1, entry 9) could be used allowing the reduction of aryl esters at temperatures from 100 °C to as low as 30 °C (Table 1, entry 14). Catalyst **4** was used in the hydrogenation of other aromatic esters with different electronic properties (Table 2). Notably, 3-pyridyl ester **16** could be successfully hydrogenated, but 2-pyridyl and 2-pyrrolyl esters were not suitable (Table 2, entries 8 and 9). A possible explanation for this fact is the ability of both ester and alcohol of the corresponding compounds to function as a bidentate N,O ligand for Ru and inhibiting catalysis. Two reactions were

set up in which the hydrogenation of ester **8** was carried out (50 °C, 50 bar H_2, 0.5 mol% cat., 25% base) in the presence of 20 mol% of either ester **17** or 2-pyridyl-CH_2OH. The reactions only gave 23 and 9% conversions, respectively, compared to full conversion without these additives. This is therefore consistent with the substrate and especially the product acting as an inhibitor.

Table 2. Hydrogenation of various methyl esters using catalyst **6**.



10: R= 4-MeC_6H_4 **14**: R= C_6H_5
11: R= 4-ClC_6H_4 **15**: R= 4-$(NH_2)C_6H_4$
12: R= 4-BrC_6H_4 **16**: R= 3-pyridyl
13: R= Napthyl **17**: R = 2-pyridyl
18: R= 2-pyrrolyl

Entry[a]	Ester	*T* [°C]	Product [%][c]
1	**10**	50	>99
2	**11**	50	>99
3	**12**	50	>99
4	**13**	50	>99
5	**14**	50	>99
6	**15**	100	0
7	**16**	100	>99
8	**17**	100	0
9	**18**	100	0

[a] Unless otherwise stated, the reactions were carried out by using 0.5 mol% of cat., *t*BuOK as base 25 mol% (50:1, base/catalyst) at an initial pressure of 50 bar with 0.4 mmol of ester in Me-THF (3 mL). [b] Conversion determined by ^{1}H NMR spectroscopy.

Next we examined the catalytic activity of the PNN and PNO Ru complexes for the hydrogenation of ethyl acetate (Table 3). Initially, to compare performance of catalysts under the same conditions, several small reactor vials were placed inside larger pressure vessels (Table 3, entries 1–5). Under 50 bar of hydrogen at 65 °C for 3 h with a 0.033 mol% of catalyst loading and in Me-THF as solvent, less than 5% conversion was achieved with phosphine diamine complex **1** and phosphine amino-amide complex **7** (Table 3, entries 4 and 5). On the other hand, both phosphine amino-alcohol-based complexes, **5** and **2**, displayed similar performance achieving the conversion of ethyl acetate to ethanol with average turnover frequencies (TOF) of 242 and 212, respectively (Table 3, entries 2 and 3).

Under the same mild conditions, the best performance was achieved using the ruthenium PNN complex **4** (Table 3, entry 1) to give a conversion of 46% and an average TOF number of 465 h^{-1}. We further investigated the activity of complex **4** in a 50 mL stainless steel, glass-lined autoclave. By using this vessel and increasing the temperature to 75 °C doubles the conversion (Table 3, entry 6). Increasing the base loading from 1.3 to 3.9 mol% (base/catalyst ratio of 118) enhanced the performance of complex **4** to produce ethanol with an average TOF number of 1131 h^{-1} (Table 3, entry 7). The ester hydrogenation reaction can also be run in neat ethyl acetate without solvent, increasing further the reaction rate (Table 3, entry 8). Complex **4** is also active at a lower catalyst loadings at 85 °C

Table 3. Optimisation studies using Ru pre-catalysts for hydrogenation of ethyl acetate.

Entry	Cat.	*t*BuOK/cat.	*t* [h]	*T* [°C]	Conv.[d] [%]	TOF [h^{-1}]
1[a]	**4**	40:1	3	65	46	465
2[a]	**5**	40:1	3	65	24	242
3[a]	**2**	40:1	3	65	21	212
4[a]	**7**	40:1	3	65	2	20
5[a]	**1**	40:1	3	65	4	40
6[b]	**4**	40:1	1.5	75	40	808
7[b]	**4**	118:1	1.5	75	56	1131
8[c]	**4**	118:1	1.5	75	71	1434
9[c][e]	**4**	240:1	1.5	85	63	2470
10[f]	**4**	118:1	1.5	75	28	566
11[c]	**5**	118:1	1.5	75	37	748

[a] The reactions were carried out by using 0.033 mol% Ru catalyst and 1.3 mol% of *t*BuOK, at an initial pressure of 50 bar using 7.7 mmol of ethyl acetate in Me-THF (3 mL) (general method A, the Supporting Information). [b] The reactions were carried out using 0.033 mol% Ru pre-catalyst, at an initial pressure of 50 bar using 30.7 mmol of ethyl acetate (3 mL) in Me-THF (3 mL) (general method B, the Supporting Information). [c] Reactions were carried out in neat ethyl acetate, otherwise using conditions as in footnote b. [d] Ethanol produced determined by ^{1}H NMR spectroscopy using 1-methylnaphthalene as internal standard. [e] 0.017 mol% of catalyst and 3.9 mol% of *t*BuOK were used. [f] Reaction carried out at constant pressure of 15 bar H_2, otherwise as in footnote b.

(Table 3, entry 9) giving a TOF of 2470 h^{-1} by using an ester to catalyst loading of 0.017 with 3.9 mol% of base. Lower pressures (15 bar) could be used in the hydrogenation of ethyl acetate although the TOF is reduced somewhat.

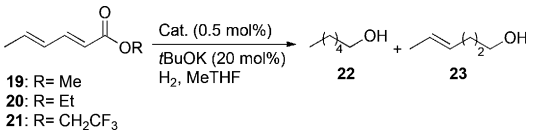
3-(*Z*)-Hexen-1-ol (leaf alcohol) occurs in the green parts of many plants and gives them the characteristic "green smell" odour. This molecule and other structural analogues are used in the perfumery industry to give a green note to fragrances. This naturally occurring homoallylic alcohol is also frequently used in the flavours industry in minty, fruity and green herbal tea aromas.[9] The reduction of the conjugated dienoate ethyl sorbate could be part of a very direct route to the fragrance molecule leaf alcohol involving a stereospecific 1,4-*cis*-hydrogenation of sorbic alcohol using [(Cp*)Ru(cod)][BF_4]-type complexes (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl; cod = 1,5-cyclooctadiene) to produce the monounsaturated alcohol with high selectivity.[9a,c] However, the chemoselective ester hydrogenation of sorbate esters to unsaturated alcohols, to our knowledge, has never been achieved, and conjugated esters remain a challenge even for the most chemoselective catalysts.[9a,10]

We attempted the hydrogenation of different sorbate esters to achieve a chemoselective reduction of the ester to produce sorbic alcohol (Table 4), but unfortunately sorbic alcohol was not observed under the reaction conditions used in this study. On the other hand, the monounsaturated alcohol **23**, possibly interesting because other isomers of leaf alcohol also possess a similar type of odour,[9b] could be obtained with moderate chemoselectivity. We first examined the influence of the ester moiety in the sorbate ester reduction using Ru catalyst **4** (Table 4, entries 1–5). The reaction using commercially available ethyl sorbate **20** afforded the highest amount of (*E*)-hex-4-en-

1-ol **23** with a 38% conversion (Table 4, entry 5). Next, we examined the performance of some of the most active catalysts (Table 4, entries 6–8). Phosphine-amino-amide catalyst **7** showed the highest selectivity towards **23** with a 51:49 selectivity (Table 4, entry 6). The use of additives (Table 4, entries 9–13) produced different results. Catalyst **7**, in the presence of 1.5 mol% of DMAP as co-catalyst (Table 4, entry 7) gave virtually no change in the selectivity of the process, but the use of PPh_3 as additive afforded compound **23** with high (80%) selectivity (Table 4, entry 13). We also examined the effect of reducing pressure and temperature on the selectivity of the reaction. By reducing the pressure to 30 bar (Table 4, entries 14–16), reducing *T* to 50 °C (entries 17–19) or by reducing both (Table 4, entries 20–22) had a different effect depending on the catalyst used in the reaction. In the case of complex **7**, the selectivity in the reaction was similar to that achieved under the initial reaction conditions (50 bar and 65 °C).

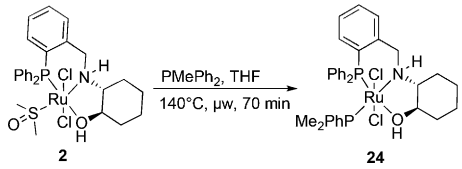
The positive effect of adding a coordinating additive to the hydrogenation has been shown to improve chemoselectivity in some cases (Table 4, entries 6 and 13). It was thought that a variation of these catalysts, in which the labile DMSO is replaced by a phosphine or DMAP, could lead to more chemoselective catalysts. We were unable to isolate any DMAP-containing complex, but we succeeded in the synthesis and isolation of the phosphine-containing counterparts. The substitution of DMSO proved to be more energetically demanding than initially expected.[11] The treatment of complex **2** with PPh_3, even when using forcing conditions (150 °C; see the Supporting Information), was very sluggish, affording the substitution complex only with 40% conversion. Next, we examined the substitution of DMSO with $PPhMe_2$; the smaller cone angle of this phosphine should facilitate the reaction. This was indeed the case and the complex was prepared under the conditions shown in Scheme 1.

Table 4. Optimisation studies using Ru pre-catalyst and sorbate esters.



Entry[a]	Ester	Cat.	*P* [bar]	*t* [h]	*T* [°C]	Conv.[b] **22** [%]	Conv.[b] **23** [%]
1	**19**	**4**	50	21	65	67	33
2	**20**	**4**	50	21	65	70	30
3	**21**	**4**	50	21	65	58	15
4	**19**	**4**	50	2	65	65	35
5	**20**	**4**	50	2	65	62	38
6	**20**	**7**	50	2	65	49	51
7	**20**	**2**	50	2	65	65	35
8	**20**	**1**	50	2	65	79	21
9[c]	**20**	**4**	50	2	65	67	33
10[c]	**20**	**7**	50	2	65	48	52
11[c]	**20**	**2**	50	2	65	16	53
12[d]	**20**	**7**	50	2	65	39	61
13[e]	**20**	**7**	50	2	65	20	80
14	**20**	**4**	30	2	65	64	36
15	**20**	**7**	30	2	65	54	46
16	**20**	**2**	30	2	65	39	61
17	**20**	**4**	50	2	50	25	37
18	**20**	**7**	50	2	50	31	55
19	**20**	**2**	50	2	50	33	67
20	**20**	**4**	30	2	50	25	37
21	**20**	**7**	30	2	50	31	55
22	**20**	**2**	30	2	50	33	67

[a] Unless otherwise stated, the reactions were carried out using 0.5 mol% of cat., *t*BuOK as base 20 mol% at an initial pressure of 50 bar using 1.0 mmol of ester in Me-THF (3 mL). [b] Conversion determined by ^{1}H NMR spectroscopy using 1-methylnaphthalene as internal standard. [c] DMAP (1.5 mol%) used as co-catalyst. [d] DBU (1.5 mol%) used as co-catalyst. [e] PPh_3 (1.5 mol%) used as co-catalyst.



Scheme 1. DMSO substitution in Ru complex **2**. The isolated pure complex **24** was obtained with 95% conversion and in 64% yield.

The $^{31}P\{^1H\}$ NMR spectrum of **24** shows two characteristic groups of doublets at $\delta = 62.4$ and 21.0 ppm with $J_{PP} = 38.1$ Hz corresponding to the two different phosphorus atoms. We then performed an X-ray diffraction study to determine unambiguously the structure of complex **24** (Figure 6). The structure confirms that $PPhMe_2$ has in fact replaced the DMSO ligand. The coordination mode around the ruthenium atoms remains broadly the same as that in complex **2**, an octahedral ruthenium complex with the tridentate neutral PNO ligand and the two chlorine atoms in apical positions. When compared with its precursor **2**, complex **24** has slightly longer Ru–N and Ru–O bond lengths (Figures 2 and 6); on the other hand, the Ru–P(1) bond is shorter (2.239(1) versus 2.256(1) Å) in complex **2**. Both complexes also show similar N-Ru-O angles: 78.8(1) in complex **24** versus 79.2(1) ° in complex **2**.

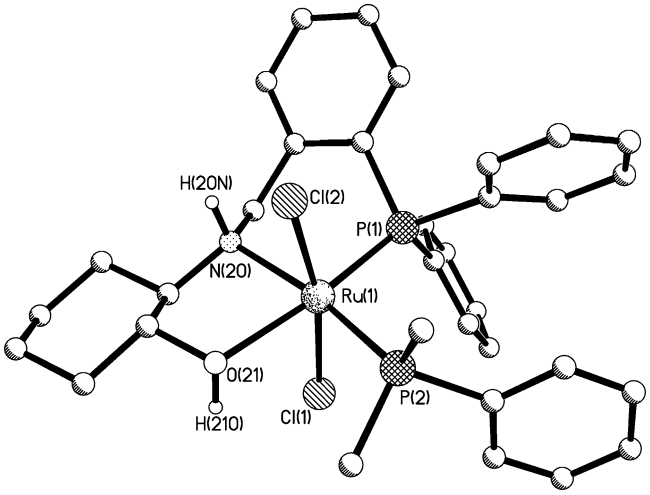
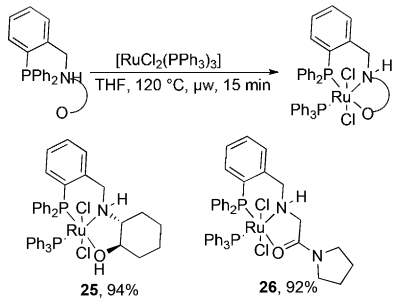


Figure 6. X-ray structure of complex **24**. THF and hydrogen atoms (except N*H* and O*H*) are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ru–P(1) 2.239(1), Ru–P(2) 2.278(1), Ru–N(20) 2.187(4), Ru–O(21) 2.236(4); O(21)-Ru-P(1) 170.3(1), N(20)-Ru-P(1) 92.0(1), O(21)-Ru-P(2) 90.5(1), P(2)-Ru-P(1) 98.89(4), N(20)-Ru-O(21) 78.8(1).

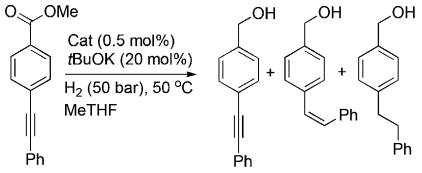
A direct synthesis involving the use of ligands (Scheme 2) and $[RuCl_2(PPh_3)_3]$ was also performed. Complexes **25** and **26** were prepared in 94 and 92% yields, respectively. The $^{31}P\{^1H\}$ NMR spectrum of **25** and **26** shows the two characteristic groups of doublets corresponding to the two different phosphorus atoms in a similar way to those of complex **24** (see the Supporting Information). These complexes were compared in a selection of ester hydrogenation reactions.



Scheme 2. Direct synthesis of complexes **25** and **26**.

The chemoselective reduction of esters in the presence of alkynes is a challenging process with several possible products being formed in the reaction and, to the best of our knowledge, no literature precedent. The main products obtained in these reductions, using methyl 4-(phenylethynyl)benzoate **27** as model substrate, are shown in Table 5. Other possible products such as methyl (*Z*)-4-styrylbenzoate and methyl 4-phenethylbenzoate would be detectable but were not observed in most cases. Compounds **28**–**30** are well-known literature compounds, and their formation can be detected by ^1H NMR spectroscopy. We decided to study the performance of the most active and selective catalysts in the presence of coordinating additives and the new phosphine-containing Ru complexes **24**–**26** in the chemoselective reduction of compound **27**. We initiated our study with complex **4** in the presence of 1 mol% of PPh_3, hoping that the presence of this phosphine could compete with the alkyne in the coordination with the metal and thus avoid the reduction of the latter (Table 5, entry 1). The reaction afforded a positive result; the alkyne formed from the selective reduction of the ester functionality (**28**) being the main product in the reaction (61% conversion after 17 h). The reaction also afforded a relative large amount of the fully reduced product (**30**). PNO Complexes **2** and **7** were also tested (Table 5, entries 6 and 9), but their selectivity towards **28** was inferior. Small amounts of alkene **29** (6–14%) were detected with all three pre-catalysts. Reducing the reaction time to 5 h increased the selectivity towards alkyne **28** (71%) with a small amount of the fully reduced product being formed (4%; Table 5, entry 2). Increasing the amount of PPh_3 did not afford any noticeable effect in the reaction (Table 5, entry 3). The use of DMAP as an additive afforded similar results to those obtained by using PPh_3 (Table 5, entry 4). Remarkably, using complex **4** with no PPh_3 present in the reaction media offered very similar chemoselectivity in the reaction (Table 5, entry 5). We also tested pre-catalysts **24**–**26**, which incorporate an extra phosphine ligand, in the reduction of **27**. The reaction proved to be very unselective towards the reduction of the ester moiety. These catalysts produced noticeable amounts of other products that were not observed before, like methyl (*Z*)-4-styrylbenzoate, the alkene obtained from the selective *cis*-reduction of **27**, and methyl 4-phenethylbenzoate, the product obtained from the full reduction of the alkyne moiety. Attempts to use complexes **24**–**26** in a *cis*-selective semi-hydrogenation of the alkyne led to significant amounts of the fully reduced alkane methyl 4-phenethylbenzoate, so these complexes were not pursued further.

Table 5. Chemoselective reduction of esters in the presence of alkynes.



27 **28** **29** **30**

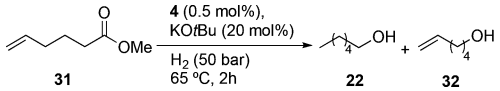
Entry[a]	Cat.	*t* [h]	**27**[b] [%]	**28**[b] [%]	**29**[b] [%]	**30**[b] [%]
1[c]	**4**	17	99	61	6	30
2[c]	**4**	5	97	71	4	4
3[d]	**4**	5	99	72	2	5
4[e]	**4**	5	99	78	9	2
5	**4**	5	98	70 (53)	6	2
6[c]	**2**	17	93	42	14	5
7[f]	**24**	5	63	9	3	0
8[g]	**25**	5	66	17	4	1
9[c]	**7**	17	87	16	10	3
10[h]	**26**	5	66	9	3	0

[a] Reactions were carried out using 0.5 mol% Ru pre-catalyst, at an initial pressure of 50 bar at 50 °C using 0.5 mmol of alkyne in Me-THF (1.5 mL) (general method A, the Supporting Information). [b] Determined by ^1H NMR spectroscopy by using 1-methylnaphthalene as internal standard; the yield of the pure isolated **28** is given in parentheses. [c] PPh_3 was used as additive (1 mol%). [d] PPh_3 was used as additive (2 mol%). [e] DMAP was used as additive (1 mol%). [f] Methyl (*Z*)-4-styrylbenzoate (21%), methyl 4-phenethylbenzoate (4%). [g] Methyl (*Z*)-4-styrylbenzoate (21%), methyl 4-phenethylbenzoate (8%). [h] Methyl (*Z*)-4-styrylbenzoate (22%), methyl 4-phenethylbenzoate (13%).

We also studied the reduction of an ester with a non-conjugated monosubstituted alkene moiety, methyl hex-5-enoate **31** (Table 6), using our best performing catalyst complex **4**. Terminal alkene-functionalised esters are more challenging substrates when compared with esters containing internal or more substituted alkenes, but less of a challenge than dienoates or α,β-unsaturated esters.[3e] The reduction proceeded with full conversion in all cases under the reaction conditions shown in Table 6, affording a mixture of both the saturated and unsaturated alcohols. Catalyst **4** gave the unsaturated alcohol as major product in all cases. The introduction of DMAP as co-catalyst had a small beneficial effect on the chemoselectivity of the ester reduction with **4**, affording unsaturated alcohol **25** with good chemoselectivity (82%, Table 6, entry 2).

Complexes **25** and **26** were also tested in the reduction of methyl hex-5-enoate **31**. These complexes did not promote

Table 6. Ru-catalysed reduction of methyl hex-5-enoate.

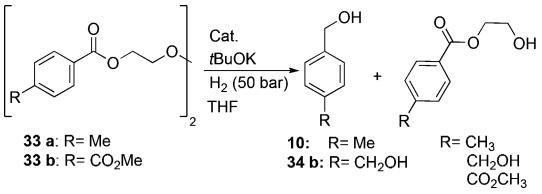


31 22 32

Entry[a]	Solvent	Conv. 31[b]	22[b] [%]	32[b] [%]
1	THF	>99	11	78
2[c]	THF	>99	10	82
3[d]	THF	>99	20	72
4	MeTHF	>99	12	77
5[c]	MeTHF	>99	13	76

[a] Unless otherwise stated, reactions were carried out using 0.5 mol% of cat., *t*BuOK as base 20 mol%, at an initial pressure of 50 bar using 0.5 mmol of ester in MeTHF (1.5 mL). [b] Conversion [%] determined by ^{1}H NMR spectroscopy using 1-methylnaphthalene as internal standard. The remaining balance is traces of isomerised internal alkene ester/alcohol. [c] DMAP was used as additive (1.5 mol%). [d] PPh_3 was used as additive (1.5 mol%).

Table 7. Ru-catalysed reduction of diesters derived from ethylene glycol.



33 a: R= Me
33 b: R= CO_2Me

10: R= Me
34 b: R= CH_2OH

R= CH_3, CH_2OH, CO_2CH_3

Entry	Substrate	Cat.	Load [mol%]	*T* [°C]	*t*BuOK/ cat.	Conv.[b] [%]	**10**[b,f] or **34 b**[b] [%]
1[a]	**33 a**	**4**	1.0	70	20:1	>99	76[f]
2[a]	**33 a**	**5**	1.0	70	20:1	>99	65[f]
3[a]	**33 a**	**2**	1.0	70	20:1	>99	60[f]
4[a,e]	**33 a**	**7**	1.0	70	20:1	>99	60[f]
5[a]	**33 a**	**4**	0.5	70	40:1	>99	>99
6[d]	**33 a**	**4**	1.0	110	20:1	>99	>99 (96)
7[a,c]	**33 b**	**4**	2.0	100	10:1	82	73[f]
8[a,c]	**33 b**	**5**	2.0	100	10:1	37	8[f]
9[a,c]	**33 b**	**2**	2.0	100	10:1	41	26[f]
10[a,c]	**33 b**	**7**	2.0	100	10:1	32	15[f]
11[a,e]	**33 b**	**4**	1.0	100	40:1	55	19[f]
12[d]	**33 b**	**4**	2.0	110	10:1	88	74[f] (71)

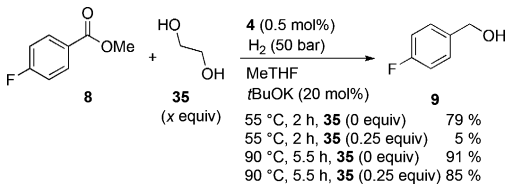
[a] Reactions were carried out at an initial pressure of 50 bar using 0.50 mmol of dimer in 3.0 mL of THF for 18 h. [b] Determined by ^{1}H NMR spectroscopy using 1-methylnaphthalene as internal standard; the yields of the isolated products are in parentheses. [c] Reaction carried out for 21 h. [d] Reaction carried out for 23 h. [e] 40:1 base to catalyst. [f] Remaining mass balance corresponds to partially reduced esters shown in the equation above.

a selective reduction of the ester and in all cases hex-5-en-1-ol **32** was not observed. The hydrogenations afforded mixtures of the product obtained from the reduction of the terminal alkene, methyl hexanoate and the fully reduced hexanol **22**, suggesting that the alkene reduction was actually promoted relative to the ester functionality under these reaction conditions.

We also considered some other related applications for our catalysts. Recently, the fundamental reactivity of ester hydrogenation catalysts has been applied towards some interesting ideas for harnessing renewable feedstocks.[12] We were attracted by the possibility of the depolymerisation of oligomers and polymers. An exciting proof-of-concept paper[12d] recently appeared in which the polyester polymer PET was depolymerised by hydrogenation to give 1,4-benzene dimethanol and ethylene glycol. This raises the possibility of a different mode of recycling: instead of melting PET and making off-white recycled polyesters, it could be recycled into chemicals that are otherwise derived from petrochemical resources. There is also a lot of PET that is currently not recycled, so this could be a good renewable feedstock. Only two examples using Milstein's catalysts are discussed in this initial work; the reactions were carried out at 160 °C and used 2 mol% of catalyst relative to the repeat unit (or 1 mol% relative to each ester). The publication of these results, which show that a step-change in reactivity would be needed prior to implementation, focused our studies on PET depolymerisation.

To identify the best catalyst and most suitable conditions and to study the effect of ethylene glycol production on the catalyst, we chose to study two model diesters first, **33 a** and **33 b**. The results are shown in Table 7; catalyst **4** emerges as the best catalyst for this transformation once again.

More forcing conditions are required even for these soluble and simple substrates relative to the conditions used in the hydrogenation of other esters in this study. To probe this further, we carried out the hydrogenation of ester **8** with varying amounts of ethylene glycol. The results (Scheme 3) show that

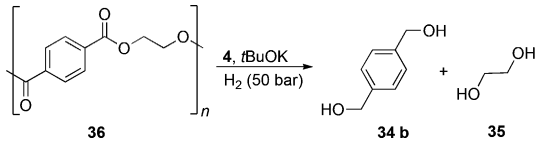


Scheme 3. Hydrogenation of ester **8** in the presence of ethylene glycol **35**.

ethylene glycol has a negative effect on the rate of this hydrogenation, at least at moderate temperatures.

With **4** identified as the best catalyst, we studied the depolymerisation–hydrogenation of real samples of waste PET. In the hydrogenation of PET flakes (Table 8), we were pleased to find that at 110 °C, a very significant conversion to benzene dimethanol was obtained by using 1 mol% catalyst relative to each ester unit (entry 1). The reaction can be performed in toluene (Table 8, entry 6), but the presence of anisole as co-solvent (as was used in ref. [12d]) is needed to increase polymer solubility (entry 5). In common with almost every report on the use of catalysis on renewable substrates, the amount of catalyst used is likely to be significantly greater than the amounts that would be needed for research leading to implementation. Because such processes are generally producing relatively low value products, the catalyst (metal and ligand) cost is critical. Further studies on new catalysts to increase the productivity beyond this new benchmark are needed.

Table 8. Depolymerisation of poly(ethylene terephthalate) (PET).



36 34 b 35

Entry[a]	Cat.	Load [mol%]	*t*BuOK/ cat.	*t* [h]	*T* [°C]	**34 b**[b] [%]
1	**4**	2.0	20:1	48	110	73 (53)
2	**4**	2.0	20:1	24	110	41
3	**4**	1.0	20:1	24	120	4
4	**4**	1.0	40:1	24	110	26
5[c]	**4**	2.0	20:1	24	110	49
6[d]	**4**	2.0	20:1	24	110	17

[a] Reactions were carried out at an initial pressure of 50 bar in a 50/50% mixture of THF/anisole. [b] Conversion determined by ^{1}H NMR spectroscopy using 1-methylnaphthalene as internal standard; yield of the isolated product is in parentheses. [c] Reaction run in a 50/50% mixture of toluene/anisole. [d] Reaction run in toluene.

Conclusion

Ten different Ru complexes of phosphine-diamine, phosphine-amino-alcohol and phosphine-amino-amide ligands have been prepared and examined in the hydrogenation of a range of esters. The simple ethylene-diamine-derived complex **4** emerges as significantly more active than the other catalysts. Complexes **2** and **5**, which are especially easy to prepare at significant scale, also give encouraging catalytic activity. Our main focus has been to establish how catalyst structure and substrate structure impact on the chemoselectivity of these ester hydrogenations; on this basis, complex **4** again outperforms other catalysts. In addition, the hydrogenation of ethyl acetate, carried out at larger scale, allows us to draw several conclusions. The average turnover frequencies observed in neat ethyl acetate are rather high relative to some of the more complex substrates. This is promising in terms of future developments with this catalyst system towards commercially viable catalyst loadings for other hydrogenations. The extra-high reactivity obtained when using the simple substrate ethyl acetate is partly because it is an easy, sterically unencumbered and very pure substrate, but also might relate to the high substrate concentrations used, since ketone hydrogenation using catalysts **4** was first order in substrate, and that is likely to be the case here. There is also a strong pressure dependence: it is possible that lower pressures could be used with a very efficiently stirred pressure vessel, but we have never been successful in carrying out ester hydrogenations at or near atmospheric pressure using these catalysts. Entries 7 and 10 in Table 3 show a significant increase in productivity when hydrogen pressure is increased from 15 to 50 bar pressure.

The effect of the base co-catalyst certainly merits discussion. Previous studies showed us that this type of catalyst was nearly inactive at these quite low temperatures if base/catalyst ratios of 2:1 are used. Some activity was observed at 140 °C. A base/catalyst ratio of around 2:1 is actually optimum for highly enantioselective ketone hydrogenation using catalyst **1**.[6] In both the hydrogenation of *para*-fluorobenzoic acid methyl ester **8** and ethyl acetate, it can be seen that activity increases significantly when the base/catalyst ratio is increased. More formally, this should perhaps be the case when the base concentration is increased, although we note experimentally that quite high concentrations were required to observe any conversion under mild conditions for the benzoate **8** (Table 1, entries 9 and 11), whereas in ethyl acetate hydrogenation, the absolute concentration of base (0.017 mol% Ru cat., 3.9 mol% base) is quite low even when average TOF are above 2000 h^{-1}. Clearly, there will be differences based on the solvating medium, the trace impurities in the substrate and the identity of the substrate. Recently, a revised mechanism has been put forward for the enantioselective hydrogenation of ketones using Noyori catalysts.[13] We have previously found our catalysts to have some mechanistic similarities to Noyori catalysts,[6c] so it seems reasonable that some of these insights might apply here. In particular, the revised mechanism postulates that the secondary alkoxide, produced after hydride transfer to a ketone, hydrogen bonds to an NH function while deprotonating a dihydrogen ligand coordinated to Ru. In ester hydrogenation, the initial product is a deprotonated hemiacetal. Hemi-acetal anions are far less basic than simple alkoxides; it may be the case that a higher concentration of base is needed either to facilitate the product deprotonating dihydrogen or to directly deprotonate dihydrogen itself. An alternative or addition role that also requires more base than in ketone hydrogenation could be required to assist the removal of bound hemi-acetal anion from ruthenium, or to assist catalyst stability.[3a] Catalyst **4** can be operated at relatively low amounts of base when catalyst loadings are low but significant amounts do seem to be needed for high productivity. This also seems to be the case for other catalysts. The effect of DMAP is somewhat mysterious, since it does not seem to be in sufficient concentration to be simply acting as more base. It was designed to act as a co-ligand for Ru that would prevent C=C bond coordination and subsequent reduction. However, we have not found it possible to make a DMAP complex in earlier studies and here we show that exchange of DMSO with a phosphine group is a difficult process, at least from the dichloride pre-catalysts. Moreover, the phosphine-ligated Ru complexes **24**–**26** are actually not just poorly active catalysts but tend to reduce the C=C bonds to a greater extent. Ru/BINAP/DPEN catalysts have also been reported to fully reduce the C=C bonds of cinnamate esters. Whether there is some outer-sphere mechanism possible for C=C reduction, or that unexpected and less saturated species form during hydrogenation is not clear. In any case, the use of catalyst **4** enables the ester hydrogenation in the presence of isolated double and triple bonds with good chemoselectivity. Catalyst **4** is therefore a useful ester hydrogenation catalyst, and we have identified some structural features and experimental protocols that appear to be beneficial for chemoselective and productive ester hydrogenation catalysis.

Experimental Section

Synthesis of ligands and catalysts along with their characterisation data can be found in the Supporting Information.

Hydrogenation of ethyl acetate using Ru catalysts

Reactions were carried out by using a Parr 50 mL stainless steel autoclave equipped with a pressure gage, gas inlet, safety valve and injection port equipped with rubber septum. A glass lined autoclave containing a magnetic stirring bar (crosshead) was charged with the appropriate amount of catalyst (0.033 mol%), purged with three vacuum/argon cycles and left under argon atmosphere. Ethyl acetate (30.7 mmol, 3.0 mL), MeTHF (3 mL) and 1-methylnaphthalene (0.2 mL) as an internal standard were added to the autoclave through the injection port using a syringe. Finally, potassium *tert*-butoxide (3.9 mol%; 1 M solution in 2-methyl-2-propanol; 1.2 mmol, 1.2 mL) was added. The autoclave was then purged three times with H_2, pressurised to 50 bar and immersed into an oil bath preheated to the desired temperature. After the desired reaction time, the autoclave was cooled down to room temperature, the pressure slowly released and opened. A small sample was taken, diluted with $CDCl_3$ and analysed by ^1H NMR spectroscopy to calculate the conversion.

Hydrogenation of methyl 4-(phenylethynyl)benzoate (27) using Ru catalysts

A Biotage 5 mL microwave vial containing a stirrer bar was charged with catalyst **4** (0.5 mol%). The vial was sealed with a crimp cap, purged with three vacuum/argon cycles and left under argon atmosphere. The corresponding ester (1.0 mmol, 236 mg) was added using a syringe from a stock solution in Me-THF containing 1-methylnaphthalene as internal standard (3.0 mL). Finally, potassium *tert*-butoxide (20 mol%; 1 M solution in 2-methyl-2-propanol; 0.2 mmol, 0.2 mL) was added, then two needles were pierced into the vial and this was introduced into an autoclave, which had been previously purged with three vacuum/argon cycles. The autoclave was then purged three times with H_2, pressurised to 50 bar and immersed into an oil bath preheated to the desired temperature. After the desired reaction time, the autoclave was cooled down to room temperature, the pressure slowly released and opened. A small sample was taken, diluted with $CDCl_3$ and analysed by ^1H NMR spectroscopy to calculate the conversion. Purification by column chromatography on silica gel using petroleum ether/EtOAc 3:1 as eluent afforded (4-(phenylethynyl)phenyl)methanol **28** as a white solid (110 mg, 0.53 mmol, 53%).

Depolymerisation of PET (36) using Ru catalyst 4

A glass insert was charged with the appropriate amount of catalyst (1–2 mol%) and substrate (1 mmol) and was introduced into an autoclave, which had been previously purged with three vacuum/argon cycles. A round bottom flask was charged with 1-methyl naphthalene (≈0.08 g) and quickly purged with three vacuum/argon cycles and left under argon atmosphere. THF (3 mL), anisole (3 mL) and potassium *tert*-butoxide (20 mol%; 1 M solution in 2-methyl-2-propanol; 0.4 mmol, 0.4 mL) were added to the round bottom flask. The solution was then added to the autoclave and the autoclave was then purged three times with H_2, pressurised to 50 bar and immersed into an oil bath preheated to the desired temperature. After the desired reaction time, the autoclave was cooled down to room temperature, the pressure slowly released and opened. A small sample was taken, diluted with $CDCl_3$ and analysed by ^1H NMR spectroscopy to calculate the conversion. Purification by column chromatography on silica gel using EtOAc as eluent afforded 1,4-benzene dimethanol **34b** as a white solid (73 mg, 0.53 mmol, 53%).

Single-crystal X-ray structural determination

CCDC 1049167 (**2**), 1049168 (**4**), 1049169 (**6**), 1049170 (**7**), and 1049171 (**24**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Keywords: bifunctional catalysis · depolymerisation · hydrogenation · ligands · ruthenium

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