

Table 1 Results of sulfur-based ruthenium catalysts in the hydrogenation of DMO^a

Entry	Ru/ μmol	Ligand	Additive (%)	Induction period/min	Substrate	Run time/h	Conversion (%)	TON ^b	TOF ^c	$k/\text{mol dm}^{-3} \text{h}^{-1}$
0	212	None	0.3	—	DMO	72	0	—	—	—
1	53	1,3,5-Trithiane	0.3	—	DMO	20	0	—	—	—
2	53	1,4,7-Trithiacyclononane	0.3	—	DMO	20	0	—	—	—
3	53	TriSulf ^{Bu}	—	>360	DMO	136	100 (MG)	100	0.74	—
4	212	TriSulf ^{Bu}	0.3	~180	DMO	23	36.9 (MG)	36.9	2.6	0.019
5	212	TriSulf ^{Bu}	0.3	~180	DMO	24	32.2 (MG)	32.2	3.4	0.024
6	212	TriSulf ^{Bu}	0.3	>200	DMO	69	87.2 (MG)	87.2	3.2	0.023
7	212	TriSulf ^{Bu}	0.3	—	MG	48	0	—	—	—
8	212	TriPhos ^{Ph}	0.3	30	DMO	5.7	100 (ED)	200	50.3	0.355
9	53	P(<i>n</i> -Oct) ₃ ^d	0.3	n/m ^d	DMO	304	100 (MG)	100	0.3	—
10	53	TriSulf ^{Bu}	0.1	—	COD ^e	28	51.6 (c-C ₈ H ₁₆) 38.4 (c-C ₈ H ₁₄)	1415.5	50.6	—

^a General conditions: 100 °C, 80 bar H₂, MeOH (30 mL), Ru(acac)₃, ligand = 1.3 equiv. to Ru, catalyst (Ru) loading 1% in all cases, Zn additive (%DMO). ^b (mol ester moiety)(mol Ru)⁻¹. ^c (mol ester moiety)(mol Ru)⁻¹ h⁻¹. ^d 6 equiv. of ligand to Ru; n/m = not measured. ^e = 1,5-Cyclooctadiene, catalyst loading 0.1%.

Ruthenium-based hydrogenation catalysts of this class, are generally observed to exhibit an induction period, between the attainment of reaction conditions and the onset of catalysis; this is widely believed to correspond to a reduction of the Ru^{III} precursor to a Ru^{II} species.¹⁰ The sulfur ligand-based catalyst system appeared to form with or without the presence of zinc, however the additive did serve to reduce the length of the induction period, and increase the rate (Table 1, entry 3 vs. 4–6). This correlates with a similar observation for the TriPhos^{Ph}-based systems.^{10,11} Significantly, the catalyst seems unable to hydrogenate DMO further than MG, as even after complete conversion to MG has occurred, prolonged reaction times see no formation of ED. To verify this, a fresh batch of catalyst was exposed to MG as substrate with no hydrogenation being evident after 48 h (Table 1, entry 7).

Analysis of the gas uptake data for these experiments reveals good reproducibility (Table 1, entries 4–6) and a reaction that is zero-order in substrate. This leads to an average zero-order rate constant of $2.2(\pm 0.2) \times 10^{-2} \text{ mol dm}^{-3} \text{ h}^{-1}$ which equates to an average TOF of $3.1(\pm 0.2) \text{ (mol ester moiety)(mol Ru)}^{-1} \text{ h}^{-1}$. In order to provide a comparison with the phosphine-based systems, runs were performed using P(*n*-Oct)₃ and TriPhos^{Ph} ligands (Table 1, entries 8 and 9) under our experimental conditions. It can be seen that the latter system gave complete conversion to ED in under 6 h, again with zero-order kinetics, leading to a calculated rate constant of $3.55 \times 10^{-1} \text{ mol dm}^{-3} \text{ h}^{-1}$; TOF of 50.3 (mol ester moiety)(mol Ru)⁻¹ h⁻¹. However, with the monodentate phosphine conversion only as far as MG was achieved, after approximately 300 h, corresponding to a TOF of 0.3 (mol ester moiety)(mol Ru)⁻¹ h⁻¹. Clearly, the TriPhos^{Ph} system is far more active, but does not stop at MG. This leads to a more meaningful comparison between TriSulf^{Bu} and P(*n*-Oct)₃ both of which are selective to MG; the former being more active. A comparison with other phosphine ligands reported in the literature,^{10**} also reveals lower rates of DMO hydrogenation to MG, than that with TriSulf^{Bu}, [e.g. TOF: PhP(C₂H₄PPh₂)₂, 2.5; (CH₂PPhC₂H₄PPh₂)₂, 2.2; PPh₃, 0.9].¹³ The ruthenium complexes of the general type Ru(CO)₂(CO₂Me)(PR₃)₂ reported by Bianchi *et al.*, also show similar or lower rates of hydrogenation to MG than the TriSulf^{Bu} system [e.g. TOF: R = Buⁿ, 3.0;⁶ R = Prⁱ, 0.6⁷].^{††} however these are not selective to MG, hydrogenating further to ED subsequently.^{5–7}

The wider applicability of this catalyst to substrates aside from esters, is illustrated by its application to the hydrogenation of 1,5-cyclooctadiene (Table 1, entry 10). At a catalyst loading of 0.1%, the substrate was converted to cyclooctane (51.6%) and cyclooctene (38.4%) in 28 h; the reaction being stopped due to time constraints rather than the catalyst losing activity. This represents a TON of 1415.5 (mol olefin moiety)(mol Ru)⁻¹ and a TOF of 50.6 (mol olefin moiety)(mol Ru)⁻¹ h⁻¹, illustrating that the TriSulf^{Bu} system hydrogenates olefins significantly faster than esters, as may have been expected.

In conclusion, the first example of a homogeneous^{‡‡} ester hydrogenation catalyst utilising a sulfur ligand has been described, which is notable for being the first example of such a catalyst not based upon phosphine ligands. The TriSulf^{Bu} system provides the most active catalyst to date that is selective towards the formation of methyl glycolate. Furthermore, this represents the first example of a simple thioether ligand in combination with ruthenium as a hydrogenation catalyst.

Notes and references

‡ The authors note that during the submission of this work a report from Milstein *et al.*²⁰ described a catalyst system that represents a step-change in performance in homogeneous ester hydrogenation. Unactivated esters are hydrogenated in a timely fashion, with good conversions at low hydrogen pressures (5.3 atm).

§ A TON of 3 is reported for the tridentate nitrogen ligand, tris(pyr-azoly)borate,^{10,11} but given a blank run also showed a single turnover, this result is not considered.

¶ The use of sulfoxide-based sulfur ligands with ruthenium for asymmetric hydrogenations of functionalised alkenes has been described.¹⁴

|| The TOF of 50.3 (mol ester moiety)(mol Ru)⁻¹ h⁻¹ determined here correlates well with that found by the original authors of 53.5 (mol ester moiety)(mol Ru)⁻¹ h⁻¹ under similar conditions.¹¹

** Very similar reaction conditions were employed: 12 mL MeOH, *p*(H₂) = 80 bar, *T* = 120 °C, Ru(acac)₃ ~20 μmol , 0.3 mol% Zn, DMO substrate, catalyst loading ~2%. The zero-order in substrate nature of this transformation allows a direct comparison of TOFs at differing catalyst loadings.

†† Values calculated from the data reported in ref. 6 and ref. 7, for the DMO to MG hydrogenation step specifically.

‡‡ No evidence of catalysis by Ru nanoclusters has been detected. Several blank experiments (see ESI)[†] were performed in the absence of ligand, colloidal Ru black being observed post-run, yet no hydrogenation activity was observed. In successful runs using the TriPhos^{Ph} or TriSulf^{Bu} ligands, Ru black formation was normally not present, a yellow/orange homogeneous solution being observed on opening the autoclave.

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