A tripodal sulfur ligand for the selective ruthenium-catalysed hydrogenation of dimethyl oxalate†

Brian Boardman, Martin J. Hanton,* Hendrik van Rensburg and Robert P. Tooze

Received (in Cambridge, UK) 26th January 2006, Accepted 13th April 2006
First published as an Advance Article on the web 2nd May 2006
DOI: 10.1039/b601216g

The first example of a catalyst utilising a sulfur-based ligand [$MeC(CH_2SBu)_3$] for the selective hydrogenation of dimethyl oxalate to methyl glycolate is reported.

The hydrogenation of esters to alcohols is a conversion of industrial importance, being employed in the production of fatty alcohols,[1,2] and being a potential route to ethane-1,2-diol *via* dimethyl oxalate.[2,3] Currently, all commercial fatty ester hydrogenation plants employ heterogeneous catalysts,[1,2] a suitable homogeneous alternative having yet to be identified. Indeed, the homogeneously-catalysed hydrogenation of esters to yield alcohols is a notoriously difficult transformation to effect, illustrated by the relative sparsity of catalysts reported for this conversion.[4–12] This prior art has been discussed previously.[11]‡

Recently, a Ru-containing system based upon a tripodal phosphine ligand, $MeC(CH_2PPh_2)_3$ ($TriPhos^{Ph}$), was described that represented a significant step forwards, providing near quantitative conversion of dimethyl oxalate (DMO) through to ethanediol (ED) at a significantly faster rate than previously reported systems (Fig. 1).[10,11] This system has also found wider application in industry.[13] However, catalysts that give conversion to methyl glycolate (MG), do so at a much reduced rate.[4–7]

Elsevier *et al.* examined a number of different ligands for this transformation with ruthenium, and concluded that a facially-capping tripodal phosphine ligand was the optimal choice.[10] In fact, phosphines are the only class of ligand reported to date, to generate an active ruthenium catalyst for this reaction.[4–13]§ Our own examination of the literature lead us to conclude that in addition to the nature of the binding mode, soft, electron-rich donor moieties are preferential.[4–13] To this end, we undertook a study of facially-capping sulfur ligands for this chemistry.

Although less widely employed than phosphines, sulfur-based ligands also have a proven track record in catalysis,[14] and in the case of sulfur macrocycles it has been suggested that these offer much improved binding of metal ions in comparison to acyclic thioethers.[15] It is noteworthy, that simple thioether-type sulfur ligands have previously found application in hydrogenation catalyst systems in combination with Rh, Pd, Ir and Pt, for unsaturated substrates, such as (functionalised) alkenes and oxygenates such as ketones, but never esters.[14]¶ Regarding tripodal sulfur ligands, $MeC(CH_2SMe)_3$ specifically,[17] has found widespread application in the coordination chemistry of transition metals,[18] including ruthenium.[19]

The commercially available sulfur macrocycles 1,3,5-trithiane and 1,4,7-trithiacyclononane were identified as suitable target ligands, whilst a tripodal scaffold was accessed *via* the synthesis of $MeC(CH_2SBu^n)_3$ ($TriSulf^{Bu}$); using a standard coupling reaction between alkyl chloride and thiol in the presence of base.[16] In an unoptimised synthesis, $MeC(CH_2Cl)_3$, excess Bu^nSH and NaOH were stirred in EtOH at 70 °C for 36 d (Fig. 2). The synthesis was inefficient, but returned the desired compound in good yield (20.3 g, 83%). Great difficulty in achieving substitution at all three arms was observed, in line with the observation of a low yield in the original report of the synthesis of $MeC(CH_2SMe)_3$.[17]

Dimethyl oxalate has been the most widely examined substrate to feature in literature reports of ester hydrogenation,[4–7] and so can be seen to represent a benchmark reaction in this type of catalysis (see Fig. 1). Furthermore, its hydrogenation to ethane-1,2-diol is of industrial interest.[3] Initial tests with the sulfur macrocycles 1,3,5-trithiane and 1,4,7-trithiacyclononane were unsuccessful, no conversion being observed (see Table 1, entries 1 and 2). Notably, no decomposition of the DMO substrate occurred, but the metal was lost as 'ruthenium-black', indicating an inability of these ligands to stabilise ruthenium under the reaction conditions, in contrast to what may have been expected.[18] However, upon application of the $TriSulf^{Bu}$ ligand in concert with a ruthenium source, successful hydrogenation was achieved through to methyl glycolate (Table 1, entries 3–6). In all cases with the $TriSulf^{Bu}$ ligand, upon opening the autoclave a transparent yellow solution was observed, with no precipitate in evidence, indicating the improved ability of the tripodal sulfur ligand to stabilise ruthenium(II) under these conditions, compared to the sulfur macrocycles.

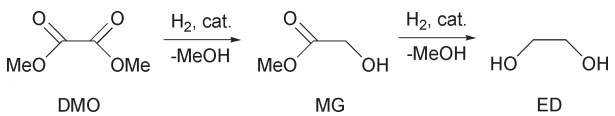

Fig. 1 The hydrogenation of dimethyl oxalate (DMO).

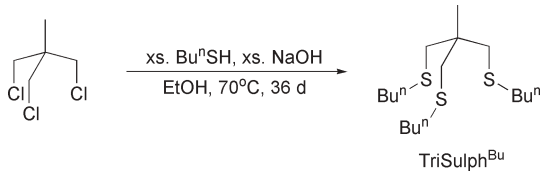

Fig. 2 The synthesis of $TriSulf^{Bu}$.

Sasol Technology UK, St Andrews Laboratory, Purdie Building, North Haugh, St Andrews, Fife, UK KY11 8FJ.
E-mail: martin.hanton@uk.sasol.com; Fax: +44(0)1707 383 647; Tel: +44(0)1334 460 830

† Electronic supplementary information (ESI) available: Experimental details, synthesis and catalysis, calculation details, kinetics. See DOI: 10.1039/b601216g

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/mol dm^{-3} 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(n-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_8H_{16}) 38.4 (c-C_8H_{14})	1415.5	50.6	—

[a] General conditions: 100 °C, 80 bar H_2, 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} mol dm^{-3} h^{-1} which equates to an average TOF of 3.1($\pm$0.2) (mol ester moiety)(mol Ru)$^{-1}$ 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} mol dm^{-3} 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($C_2H_4PPh_2$)$_2$, 2.5; ($CH_2PPhC_2H_4PPh_2$)$_2$, 2.2; PPh_3, 0.9].[13] The ruthenium complexes of the general type Ru(CO)$_2$(CO$_2$Me)(PR$_3$)$_2$ reported by Bianchi *et al.*, also show similar or lower rates of hydrogenation to MG than the TriSulf^{Bu} system [*e.g.* TOF: R = Bu^n, 3.0;[6] R = Pr^i, 0.6[7]]†† 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(pyrazolyl)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, $p(H_2)$ = 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.

1 R. F. Modler, R. Gubler and Y. Inoguchi, Detergent Alcohols, *CEH Marketing Research Report*, 2004; W. S. Fong, Natural Detergent Alcohols by a Vapour Phase Ester Hydrogenation Process, *PEP Review 93-2-1*, 2004.

2 N. W. Cant, D. L. Trimm and T. Turek, *Catal. Rev. Sci. Eng.*, 1994, **36**, 645–683.

3 J. Lacson, Mono-, Di- and Tri-ethylene Glycols, *CEH Product Review*, 2003.

4 R. A. Grey, G. P. Pez and A. Wallo, *J. Am. Chem. Soc.*, 1981, **103**, 7536–7542; R. A. Grey, G. P. Pez, J. Corsi and A. Wallo, *J. Chem. Soc., Chem. Commun.*, 1980, 783–784; R. A. Grey and G. P. Pez, Allied Chemicals, US 4232170, 1980; R. A. Grey and G. P. Pez, *Fundam. Res. Homogeneous Catal.*, 1984, **4**, 97–116; R. A. Grey and G. P. Pez, *Prepr. - Am. Chem. Soc., Div. Pet. Chem.*, 1980, **25**, 399–403.

5 U. Matteoli, G. Menchi, M. Bianchi, F. Piacenti and P. Frediani, *J. Mol. Catal.*, 1984, **22**, 353–362; U. Matteoli, G. Menchi, M. Bianchi, P. Frediani and F. Piacenti, *J. Mol. Catal.*, 1985, **29**, 269–270; U. Matteoli, G. Menchi, M. Bianchi and F. Piacenti, *J. Mol. Catal.*, 1988, **44**, 347–355; U. Matteoli, G. Menchi, M. Bianchi, F. Piacenti, S. Ianelli and M. Nardelli, *J. Organomet. Chem.*, 1995, **498**, 177–186.

6 U. Matteoli, G. Menchi, M. Bianchi and F. Piacenti, *J. Organomet. Chem.*, 1986, **299**, 233–238.

7 U. Matteoli, G. Menchi, M. Bianchi and F. Piacenti, *J. Mol. Catal.*, 1991, **64**, 257–267.

8 K. Nomura, H. Ogura and Y. Imanishi, *J. Mol. Catal. A: Chem.*, 2001, **166**, 345–349; K. Nomura, H. Ogura and Y. Imanishi, *J. Mol. Catal. A: Chem.*, 2002, **178**, 105–114.

9 Y. Hara, H. Inagaki, S. Nishimura and K. Wada, *Chem. Lett.*, 1992, 1983–1986.

10 M. C. van Engelen, H. T. Teunissen, J. G. De Vries and C. J. Elsevier, *J. Mol. Catal. A: Chem.*, 2003, **206**, 185–192.

11 H. T. Teunissen and C. J. Elsevier, *Chem. Commun.*, 1997, 667–668.

12 H. T. Teunissen and C. J. Elsevier, *Chem. Commun.*, 1998, 1367–1368.

13 M. Kilner, D. V. Tyers, S. P. Crabtree and M. A. Wood, Davy Process Technology, WO 03/093208 A1, 2003.

14 J. C. Bayón, C. Claver and A. M. Masdeu-Bultó, *Coord. Chem. Rev.*, 1999, **193–195**, 73–145.

15 S. J. A. Pope, N. R. Champness and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1997, 1639–1644.

16 M. Konrad, F. Meyer, K. Heinze and L. Zsolnai, *J. Chem. Soc., Dalton Trans.*, 1988, 199–205.

17 R. Ali, S. J. Higgins and W. Levason, *Inorg. Chim. Acta*, 1984, **84**, 65–69.

18 A. J. Barton, J. Connolly, W. Levason, A. Mendia-Jalon, S. D. Orchard and G. Reid, *Polyhedron*, 2000, **19**, 1373–1379; W. Levason, B. Patel and G. Reid, *Inorg. Chim. Acta*, 2004, **357**, 2115–2120; N. J. Hill, W. Levason and G. Reid, *Inorg. Chem.*, 2002, **41**, 2070–2076; P. J. Schebler, C. G. Riordan, I. A. Guzei and A. L. Rheingold, *Inorg. Chem.*, 1998, **37**, 4754–4755.

19 W. Levason, S. D. Orchard and G. Reid, *J. Chem. Soc., Dalton Trans.*, 2000, 4550–4554.

20 J. Zhang, G. Leitus, Y. Ben-David and D. Milstein, *Angew. Chem., Int. Ed.*, 2006, **45**, 1113–1115.