Electronic Supplementary Information

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

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

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

Table of Contents

General Information

All chemicals were purchased from standard commercial sources and used as received. NMR spectra were collected on a Bruker Avance 300MHz, at ambient probe temperature. Chemical shifts were referenced to residual protio impurities in the deuterated solvent (^{1}H) or the ^{13}C shift of the solvent (^{13}C). Chemical shifts are reported in ppm and coupling constants in Hz. GC-MS analysis was performed using an Agilent Technologies 6890N GC unit (column = Supelco MDN35, 30m × 0.25 mm × 0.25µm) coupled to a 5973N mass spectrometer. GC analysis was performed using an Agilent Technologies 6890N GC unit (column = Supelco MDN35, 60m × 0.25 mm × 0.25µm).

1,1,1-*tris*(*n*-Butylthiomethyl)ethane, $MeC(CH_2SBu)_3$, TriSulph^{Bu}

A 3 L RBF equipped with reflux condenser, scrubbing chain[1] and stirrer bead was charged with EtOH (300 mL), NaOH (8.690 g, 2.17×10^{-1} mols) and *n*-butylthiol (35.0 mL, 3.26×10^{-1} mols), and cooled to 0^{o}C. An EtOH (150 mL) solution of 1,3-dichloro-2-chloromethyl-2-methylpropane (10 mL, 7.24×10^{-2} mols) was then added to the stirred, cooled solution and the vessel left to warm to RT overnight. After this time the colourless solution had undergone no colour change, and a slight white precipitate was present. The vessel was heated to 70^{o}C in steps and the vessel stirred overnight – copious white precipitate resulted. GC-MS analysis showed good formation of mono-substituted material, but no di- or tri- substituted product. Significant quantities of Bu_2S_2 and Bu_2S were present.

Over the next 36 days, a further 17 aliquots of NaOH (8.690 g, 2.17×10^{-1} mols) and *n*-butylthiol (35.0 mL, 3.26×10^{-1} mols) were added to the vessel at roughly 2-3 day intervals, plus a further 200 mL of EtOH, and the stirred vessel maintained at 70^{o}C throughout. A dark orange solution and copious white precipitate resulted. After this time, the vessel was cooled to RT and cyclohexane (~300 mL) added to further precipitate salts. The solution was filtered and the solids washed with cyclohexane (2 × 100 mL). The organic solution was then reduced *in vacuo* to leave a thick orange oil and white solid. This material was dissolved in a mixture of water (~1 L) and cyclohexane (~1 L), vigorously shaken and allowed to separate on standing. A yellow organic layer and orange aqueous layer resulted. The yellow layer was collected and analysed to show Bu_2S_2, Bu_2S, di- and tri-substituted product (1.8% vs. 98.2% respectively). Upon analysis the orange layer was shown to contain only traces of the desired product.

---

[1] A scrubbing chain consisting of 4 × 1 L Dreschel bottles, the middle two being filled with a saturated aqueous solution of $CuSO_4$, was fitted to the reaction vessel exit, and the vessel itself operated as a sealed system under a N_2 blanket. *n*-Butylthiol, and the corresponding disulphide and thioether are highly olfactory active compounds and should be handled with care and disposed of responsibly. Bleach proved effective for the destruction of these compounds after extended periods (1 month +). .

The organic solution was reduced *in vacuo* to leave ~ 100 mL of an orange oil. This material was subjected to a short path distillation (see table below). Fraction D3 was retained as product, pale yellow oil, 20.270 g (83% yield, purity[2] 97.9%, remaining 2.1% di-substituted material).

Fraction	Boiling range	Volume	Analysis
D1	< 100°C @ 0.25 mmHg	~70	$\mathrm{Bu_2S_2}$ 100%
D2	< 125°C @ 0.05 mmHg	~1	$\mathrm{Bu_2S_2}$ 70%, ~10% mono-, ~10% di-, ~10% unknown
D3	< 163°C @ 0.01 mmHg	~25	97.9 % tri-, 2.1 % di- substituted product.
POT	undistilled residue	~2	Not analysed

^{1}H (300.06 MHz, $\mathrm{CDCl_3}$) δ: 2.64 (6H, s, $\mathrm{H_3CC\{C\mathit{H}_2SCH_2CH_2CH_2CH_3\}_3}$), 2.52 (6H, t, $^3J_{HH}$ = 7.3 Hz, $\mathrm{H_3CC\{CH_2SC\mathit{H}_2CH_2CH_2CH_3\}_3}$), 1.55 (6H, *ps*-quin, $^3J_{HH}$ = 7.0 Hz, $\mathrm{H_3CC\{CH_2SCH_2C\mathit{H}_2CH_2CH_3\}_3}$), 1.40 (6H, *ps*-quin, $^3J_{HH}$ = 7.0 Hz, $\mathrm{H_3CC\{CH_2SCH_2CH_2C\mathit{H}_2CH_3\}_3}$), 1.07 (3H, s, $\mathrm{\mathit{H}_3CC\{CH_2SCH_2CH_2CH_2CH_3\}_3}$), 0.89 (9H, t, $^3J_{HH}$ = 7.4 Hz, $\mathrm{H_3CC\{CH_2SCH_2CH_2CH_2C\mathit{H}_3\}_3}$).

^{13}C {^{1}H} (75.46 MHz, $\mathrm{CDCl_3}$) δ: 42.20 (s, $\mathrm{H_3CC\{\mathit{C}H_2SCH_2CH_2CH_2CH_3\}_3}$), 40.81 (s, $\mathrm{H_3C\mathit{C}\{CH_2SCH_2CH_2CH_2CH_3\}_3}$), 34.21 (s, $\mathrm{H_3CC\{CH_2SCH_2\mathit{C}H_2CH_2CH_3\}_3}$), 32.42 (s, $\mathrm{H_3CC\{CH_2S\mathit{C}H_2CH_2CH_2CH_3\}_3}$), 24.21 (s, $\mathrm{H_3\mathit{C}C\{CH_2SCH_2CH_2CH_2CH_3\}_3}$), 22.37 (s, $\mathrm{H_3CC\{CH_2SCH_2CH_2\mathit{C}H_2CH_3\}_3}$), 14.10 (s, $\mathrm{H_3CC\{CH_2SCH_2CH_2CH_2\mathit{C}H_3\}_3}$).

MS ($\mathrm{EI^+}$): 336 $(\mathrm{M})^+$ [isotope pattern matched with theory], 279 $(\mathrm{M\text{-}Bu^n})^+$, 247, $(\mathrm{M\text{-}SBu^n})^+$, 133 $(\mathrm{M\text{-}SBu^n\text{-}Bu^n\text{-}Bu^n})^+$.

Catalysis – Experimental Details

Catalytic tests were performed under a standard set of conditions: 100°C, 80 bar $\mathrm{H_2}$, 30 mL MeOH solvent. The runs using 53 μmol of Ru were performed as screening runs, in a 50 mL batch autoclave charged to 80 bar $\mathrm{H_2}$; the vessel pressure fell with gas consumption to as low as 70 bar; no attempt was made to log gas uptake and no samples were taken during the run. The runs using 212 μmol of Ru were performed on a kinetic rig: a 50 mL batch autoclave equipped with ballast vessel and sampling device; the autoclave pressure was maintained at 80 bar throughout the reaction *via* mass-flow controller, and the gas uptake from the ballast vessel logged; the gas uptake data was corrected for pressure drops due to sampling. Samples for GC analysis were taken during and at the end of runs.

TON's reported are in terms of (mols of ester moiety)(mol Ru)$^{-1}$, so conversion of one molecule of DMO to ED represents, two turnovers. Where a zero-order rate constant was determined (212 μmol Ru runs; see below for kinetics information), this was used to calculate TOF, otherwise the TON was divided by the run time. The run times cited are the duration the run was performed for, unless complete conversion of the substrate was achieved in less time, in which case this value is used. The experiments reported (Table 1 entries, main paper) are individual runs and not the average of several runs. In the case of entries 4-6 which were duplicates to illustrate reproducibility, an averaged rate constant and TOF are quoted. The error in this value is simply the standard error calculated based upon averaging the three values.

---

[2] Purity was measured by comparison of ^{1}H NMR signals for the di- and tri-substituted products.

The analysis of catalytic runs looked for conversion to desired products, but also the formation of unwanted by-products, arising from hydrolysis of the ester to acid (by trace water) or transesterification reactions between compounds present. The conversions quoted are based upon response factor corrected GC integrations, and in the case of GC-MS analysis, response factor corrected integrations, the response factors being determined in the approximate concentration range the samples were analysed.

A series of blank experiments were performed, in addition to the single entry in the manuscript (Table 1, entry 0); in all cases no conversion was observed. See below.

Ru / μmol	Ligand	Additive (%)	Substrate	Run time / hr	Conversion (%)	Comments
0	none	-	DMO	16	0	No decomposition of substrate observed
0	none	0.3	DMO	16	0	No decomposition of substrate observed
0	TriPhos^{Ph}	0.3	DMO	16	0	No decomposition of substrate observed
212	none	0.3	DMO	23	0	No decomposition of substrate observed
212	none	-	DMO	72	0	No decomposition of substrate observed

General conditions: 100°C, 80 bar H_2, MeOH (30 mL), $Ru(acac)_3$, ligand = 1.3 eq to Ru, catalyst (Ru) loading 1% in all cases, Zn additive.

Kinetics Calculations

The data between 20% and 80% conversion was used for rate calculations, an adherence to zero-order kinetics being evident during this range. If 80% conversion was not reached before an experiment was stopped the observed period of adherence to zero-order kinetics was examined. The gas uptake data was correlated with the concentration of substrate remaining in solution at time t. A plot of this concentration against time (hr) gave a straight line, with gradient, *k*, the zero-order rate constant in mol (ester) dm^{-3} hr^{-1}. The TOF was derived from this value *via* division by the catalyst concentration.