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Catalytic Deoxydehydration of Diols to Olefins by using a Bulky Cyclopentadiene-based Trioxorhenium Catalyst

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A bulky cyclopentadienyl (Cp)-based trioxorhenium compound was developed for the catalytic deoxydehydration of vicinal diols to olefins. The 1,2,4-tri(*tert*-butyl)cyclopentadienyl trioxorhenium (**2**) catalyst was synthesised in a two-step synthesis procedure. Dirhenium decacarbonyl was converted into 1,2,4-tri(*tert*-butyl)cyclopentadienyl tricarbonyl rhenium, followed by a biphasic oxidation with H_2O_2 . These two new three-legged compounds with a 'piano-stool' configuration were fully characterised, including their single crystal X-ray structures. Deoxy-dehydration reaction conditions were optimised by using

Introduction

Because of the increasing need for energy and material sources, biomass is currently considered as an alternative resource for the sustainable production of chemicals, fuels, and energy. In this respect, biomass-derived feedstocks, such as sugars and polyols, are interesting starting materials to replace conventional oil resources,^[1] which are further depleting and concomitantly increasing in price. Unlike oil-derived hydrocarbons, the sugar derivatives are oxygen-rich materials because of the high abundance of hydroxyl groups. The main challenge in utilising such oxygen-rich materials is to reduce their oxygen content and, accordingly, decrease their polarity. In particular, this approach will yield olefins, which are essential chemicals for both the polymer and the bulk chemical industries.^[2]

The production of olefins from sugars and sugar-derived polyols is viable through deoxygenation^[3] and dehydration,^[4,5] or combinations of these reactions, such as di-dehydroxylation^[6] or deoxydehydration reactions.^[7–12] Although alcohol dehydrations are well-known acid-catalysed and high-temperature transformations,^[13] transition-metal-catalysed versions of these reactions have been studied to a lesser extent. We recently reported rhenium-catalysed dehydration reactions of benzylic, non-benzylic, and biobased alcohols.^[5] Amongst the transition metal catalysts currently known for these transforma-

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beoxyusing derived polyols (glycerol and erythritol) were converted into using their corresponding olefinic products by **2** as the catalyst. sourtions, rhenium-based catalysts seem best suited because of the facile bond-forming and bond-breaking tendency of rhenineray um-oxygen bonds ^[14] In an early study Cook and Andrews re-

the facile bond-forming and bond-breaking tendency of rhenium-oxygen bonds.^[14] In an early study, Cook and Andrews reported the catalytic deoxydehydration of polyols into olefins by using Cp*ReO₃ as the catalyst (Cp*=1,2,3,4,5-pentamethylcyclopentadienyl).^[7] 2 mol% catalyst loading was used in combination with triphenylphosphine as a stoichiometric reductant to achieve quantitative conversion of phenylethane-1,2-diol into styrene in chlorobenzene at 90 °C. Later, Gable and coworkers used Tp*ReO₃ [Tp*=hydrido-tris-(3,5-dimethylpyrazolyl)borate] as an alternative catalytic system by replacing the Cp* with a Tp* ligand.^[15] Nevertheless, the total turnover number was limited in both cases.

2 mol% loading of **2** for the conversion of 1,2-octanediol into 1-octene. Different phosphine-based and other, more conven-

tional, reductants were tested in combination with 2. Under

optimised conditions, a variety of vicinal diols (aromatic and

aliphatic, internal and terminal) were converted into olefins in

good to excellent yields, and with minimal olefin isomerisation.

A high turnover number of 1400 per Re was achieved for the

deoxydehydration of 1,2-octanediol. Furthermore, the biomass-

The proposed deoxydehydration mechanism of these catalysts involves initial reduction of LRe^{VII}O₃ to obtain the active species, $LRe^{V}O_{2}$ (in which L = ligand). Next, condensation of the diol substrate with LRe^VO₂ leads to the diolate intermediate, followed by a thermal cycloreversion through which the olefin product is released.^[7] Herrmann et al. had earlier reported the formation of Re^V diolate intermediates and successive possible extrusion of olefin products for their Cp*ReO₃ catalyst.^[16] Furthermore, Gable and co-workers developed new routes to synthesise different Re^v diolates and investigated the mechanistic pathways of the cycloreversion reactions in detail by using kinetic studies.^[17] One of their findings was that the very active dioxorhenium (LRe^VO₂) species, formed upon reduction of the starting trioxo complex, is in equilibrium with its dimeric form. In addition, over-reduction of the dioxo complex leads to the formation of catalytically inactive Re^{III} species. Each of these events results in catalyst deactivation and lower turnover numbers per rhenium atom.

The versatile oxidation catalyst $\mathsf{CH}_3\mathsf{ReO}_3$ (MTO) was also used for deoxydehydration reactions in combination with

a number of different reductants, including molecular hydrogen,^[8] Na₂SO₃,^[9,10] and alcohols.^[11,12] Very recently, independent works by Yi et al.^[11] as well as Shiramizu and Toste^[12] showed the catalytic conversion of polyols into olefins by using MTO and secondary alcohols as both the reductant and solvent. In addition, Yi et al. reported that the substrate itself, that is, glycerol, could be used as the reductant to obtain C₃ volatile products in a distillation set up at 165 °C. Shiramizu and Toste documented the conversion of biomass-derived sugars and polyols into furan derivatives or aromatics, and linear polyenes, respectively.

Results and Discussion

In the development of improved deoxydehydration catalysts based on rhenium, we envisioned the use of robust cyclopentadienyl (Cp)-based catalysts by considering both the electronics and the steric bulk of the ligand system. Amongst a series of Cp-derived ligands, the Cp* ligand can be compared to the 1,2,4-tri(*tert*-butyl)cyclopentadienyl ligand in terms of electronics, whereas the latter is bulkier than the former. Herein, we present the development of the 1,2,4-tri(*tert*-butyl)cyclopentadienyl-based trioxorhenium complex as a proficient catalyst for deoxydehydration reactions.

We started our investigation to synthesise 1,2,4-tri(*tert*-butyl)cyclopentadienyl trioxorhenium (**2**) by utilising literature methods for the two-step synthesis of Cp-based trioxorhenium complexes (Scheme 1). 1,2,4-Tri(*tert*-butyl)cyclopentadiene was synthesised according to the literature procedure reported by



Scheme 1. Synthetic scheme for the formation of 1 and 2.

Sitzmann and co-workers.^[18] Similar to the procedure reported by Patton et al.,^[19] an excess of substituted cyclopentadiene was mixed with dirhenium decacarbonyl and refluxed in neat conditions under a nitrogen atmosphere to generate the tricarbonyl complex. Gradual heating of the reaction mixture from 150 to 210 °C led to complete conversion of the rhenium starting material, yielding 42% of the tricarbonylrhenium complex (1). After a simple work-up by washing away the excess ligand with cold hexane, **1** was obtained in a pure form according to NMR spectroscopy. Singlet peaks at 5.35 (2H, Cp–H), 1.37 (18H, *t*Bu), and 1.19 ppm (9H, *t*Bu) were observed by using ¹H NMR spectroscopy, in addition to a peak at 196.61 ppm in ¹³C NMR spectroscopy, which corresponded to one unique carbonyl environment. Two strong IR vibrational modes were observed at 1886 (ν_{asym}) and 2004 cm⁻¹ (ν_{sym}) for the carbonyl moiety. Electrospray ionisation mass spectrometry (ESI-MS) showed an ion with an *m/z* value of 504.1729, corresponding to a [M]⁺ cationic species (calcd *m/z*=504.1675).

Next, 1 was oxidised to obtain the corresponding trioxorhenium compound, 2, by using a well-established biphasic oxidation method. $^{\scriptscriptstyle [20]}$ 1 was refluxed for 15 h in a benzene solution in the presence of H₂O₂ (31 equiv., 35% in water) under a nitrogen atmosphere to yield the product as a yellow crystalline material in 73% yield after work-up. A few drops of concentrated H₂SO₄ were added to the reaction mixture to activate H₂O₂ for the oxidative decarbonylation of the starting material, as described by Herrmann and co-workers as well as Wallis and Kochi.^[20,21] Clear downfield shifts were observed for the Cp hydrogen (from 5.35 to 6.55 ppm) and the carbon signals in the NMR analysis, and the disappearance of the carbonyl peak in the ¹³C NMR spectrum indicated clean conversion of 1 to 2. Typical Re=O IR vibrations at 877 (ν_{asym}) and 917 cm⁻¹ (ν_{sym}), as well as the absence of carbonyl vibrations, further evidenced the formation of 2. By using ESI-MS, two cationic species were observed; one at m/z = 469.1753 for $(M+H)^+$ (calcd m/z =469.1683) and one at m/z = 532.1820 for $(M + Na + CH_3CN)^+$ (calcd *m*/*z* = 532.1832).

Compounds 1 and 2 crystallized from a 2:1 mixture of dichloromethane and hexane at -30 °C. The molecular structures exhibit typical three-legged 'piano-stool' configurations, similar to other known Cp-based rhenium compounds (Figure 1). The OC-Re-CO angles in 1 are between 89.18(9) and 90.84(7)°, the C-C (Cp) distances are in the range 1.420(2)-1.472(2) Å, and the Re to Cp (centroid) distance is 1.9569(7) Å. The C-C(Cp) distances in 2 are in the range 1.408(3)-1.450(2) Å. This indicates a slight decrease in the C-C bond lengths in the substituted Cp-ring as a consequence of the oxidation of carbonyl compound 1 into oxo-compound 2. Such a shortening has previously been reported in the literature.^[20,22] In 2, the Re to Cp (centroid) distance is 2.0830(8) Å, the Re=O distances are between 1.7239(15) and 1.7267(14) Å, and the O=Re=O angles are between 103.86(8) and 105.39(8) $^{\circ}$. The orientation of the tBu groups in 2 is anticipated to be beneficial in shielding the ReO₃ moiety.

We started our catalytical investigations by using **2** for the deoxydehydration of vicinal diols into olefins with 1,2-octanediol as a substrate (Scheme 2). Initial catalytic reactions were performed with 2 mol% catalyst **2** at 180 °C in chlorobenzene with 1.1 equiv. triphenylphosphine as the reductant under an inert nitrogen atmosphere, that is, under similar conditions to those previously reported by Cook and Andrews for Cp*ReO₃ in this reaction.^[7] A profile of the reaction over time showed that it proceeded to completion within 15 h, and exclusively yielded octenes (1-octene/2-octene = 1:0.05; Figure 2). Performing the reaction under aerobic conditions resulted in moderate octene formation (60%) at 75% conversion.

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Figure 1. Displacement ellipsoid plot of complex 1 and 2 in the crystal at 50% probability. Hydrogen atoms are omitted for clarity.



Scheme 2. Conversion of 1,2-octanediol into octenes catalysed by 2.

To reduce the formation of 2-octene, the reaction temperature was lowered. At 150 and 135 °C, complete conversion of 1,2-octanediol was observed and octene yields were very good (Table 1, entries 2 and 3). The amount of 2-octene isomers was lower when the reaction was performed at 135 °C compared to the amount produced at 180 °C. At 150 °C, the amount of 2-octenes (12.4%; *trans/cis* ratio = 0.51/1) was relatively high. This was attributed to the isomerisation of 1-octene into 2-octenes under the reaction conditions, that is, at longer reaction times. When the reaction was performed below the reflux temperature of chlorobenzene, moderate to low yields were obtained (Table 1, entries 4–7). At 130 °C, 1-octene was obtained in good yield within 15 h and complete conversion was observed after 24 h (91% 1-octene). Poor conversions and yields were ob-



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Figure 2. Reaction profile of the deoxydehydration of 1,2-octanediol catalysed by using 2 at 180 $^\circ$ C.

Table 1. Optimisation of the reaction temperature for the conversion of 1,2-octanediol into octenes catalysed by $\mathbf{2}^{[a]}$

Entry	<i>Т</i> [°С]	1-octene	Yield [%] ^[b] trans-2-octene	cis-2-octene	Conversion ^[b] [%]	t [h]			
1 2 3 4 5 6 7 ^[d]	180 150 135 130 120 110 100	89 79 94 80 ^[c] 26 6 11	3 4.2 1.3 0 0 0 0	3 8.2 1 0 0 0 0	> 99 > 99 > 99 86 35 10 18	15 15 12 15 15 15 38			
[a] Reaction conditions: 1,2-octanediol (0.5 mmol), 2 (0.01 mmol), PPh_3 (0.55 mmol), PhCl (5 mL). [b] Determined by using GC with mesitylene (0.5 mmol) as an internal standard. [c] 91% 1-octene at complete conversion after 24 h. [d] No trace of octene after 12 h.									

tained in the temperature range 100–120 °C. No significant improvement in conversion was observed at 100 °C upon extension of the reaction time to 38 h. Interestingly, at lower temperatures, isomerisation did not occur and 1-octene was obtained selectively.

Next, a number of different apolar and polar solvents were tested for the reaction at their respective reflux temperature. The reaction performed in toluene resulted in a moderate yield, whereas in benzene it produced a very low yield (Table 2, entries 2 and 3). In more polar and coordinating solvents, such as tetrahydrofuran (THF) and acetonitrile, no significant reactivity was observed. When the reactions were performed at 180°C in pressure tubes in these solvents, much better conversions and yields were obtained for the non-polar solvents, producing >90% octene products after complete conversion of the substrate (entries 1-3). In this case, 2-octene isomers were also obtained at a higher trans/cis isomer ratio (\approx 2:1) in non-polar solvents, whereas more of the *cis* isomer was formed in THF (entry 4). In acetonitrile, no reaction was observed, even at 180 °C (entry 5). It is likely that acetonitrile coordination to rhenium prevented the reaction from taking place. Interestingly, another coordinating basic solvent, pyri-

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Table 2. Solvent optimisation for the deoxydehydration of 1,2-octanediol catalysed by 2. ^[a]										
Entry	Solvent	1-octene	Yield [%] ^[b,c] trans-2-octene	cis-2-octene	Conversion ^[b, c] [%]	1-octene	Yield [%] ^[c,d] trans-2-octene	cis-2-octene	Conversion ^[c, d] [%]	
1	PhCl	94	1.3	1	> 99	89	3	3	> 99 ^[e]	
2	toluene	34	0	0	36	83	7.7	5.8	>99	
3	benzene	2	0	0	16	84	4.7	3.1	>99 ^[f]	
4	THF	trace			11	84	2.3	5.3	>99 ^[e]	
5	CH ₃ CN	trace			5	trace			9	
6	pyridine	2	0	0	8	67	0	0	83	
[a] React	tion condition	ns · 1 2-octane	diol (0.5 mmol) 2	(0.01 mmol) PPh	(0.55 mmol) solve	nt (5 ml) 15	h [h] At reflux tem	perature for 15 h	[c] Determined	

[a] Reaction conditions: 1,2-octanediol (0.5 mmol), 2 (0.01 mmol), PPh₃ (0.55 mmol), solvent (5 mL), 15 h. [b] At reflux temperature for 15 h. [c] Determined by using GC with mesitylene (0.5 mmol) as an internal standard. [d] At 180 °C for 15 h, unless otherwise stated. [e] 12 h. [f] 17 h.

dine, produced a 67% yield of 1-octene at 83% conversion of 1,2-octanediol at 180°C (entry 6), whereas a similar trend of very poor conversion was observed at 135°C. The reactivity in pyridine could be of interest for the conversion of very polar polyol substrates because of solubility reasons.

As a next step in protocol optimisation, the use of alternative reductants to triphenylphosphine was investigated. Other phosphines such as electron-rich P(*n*Bu)₃ and PCy₃ or electron-deficient P(C₆F₅)₃ provided very poor conversions and produced less than 5% 1-octene at 135 °C (Table 3, entries 2A-4A). Interestingly, the use of these phosphines at 180 °C significantly improved the overall reactivity (entries 2B and 3B). PCy₃ produced an overall octene yield of 94%, including 2-octenes (14%; *trans/cis* ratio = 0.43:1) at complete conversion of 1,2-octanediol. P(C₆F₅)₃ produced only 47% 1-octene at 54% conversion over 12 h. A poor yield was obtained with P(*n*Bu)₃, which was attributed to very fast catalyst deactivation (entry 4).^[23]

The use of other conventional reductants also resulted in a poor overall reactivity at $135 \,^{\circ}$ C (entries 5A–8A). Sodium sulfite resulted in a very poor conversion, which was most likely because this salt does not dissolve in chlorobenzene (entry 5). The use of molecular hydrogen (40 bar) resulted in 21% *n*-

octane formation (as the over-reduced product) at 35% substrate conversion.^[24] Increasing the temperature from 135 to 180°C clearly led to an improved yield (47%) at complete conversion. Changing the solvent from chlorobenzene to THF yielded a mixture of octene isomers and octane products in poor yield at 135 °C, whereas at 180 °C the activity increased with an increased formation of 2-octene isomers (entry 6). By using the secondary alcohol 3-pentanol or the substrate itself as the reductant, poor yields were obtained (entries 7-8). At 180°C, moderate yields were obtained in both cases within 15 h. Interestingly, 100% selectivity (50% yield) of 1-octene was achieved by the consumption of 50% of substrate as the reductant through hydrogen transfer, as reported by Yi et al. (entry 8).^[11] These experimental observations are in accordance with the rate-determining step involving the cycloreversion of the diolate intermediate at elevated temperatures, which was studied by Gable and co-workers^[17] and in recent independent density functional theory (DFT) calculations by Bi et al., Qu et al., and Liu et al..^[25]

Following these optimisation studies, the substrate scope was investigated by using a variety of vicinal diols under optimised reaction conditions, that is, 1.1 equiv. PPh₃, chloroben-

Tab	le 3. Re	eductant variati	on for th	e deoxydehydratio	n of 1,2-octanediol	catalysed by 2 . ^{[a}	a]	
Ent	ry	Reductant	<i>T</i> [°C]	1-octene	Yield [%] ^[b] trans-2-octene	cis-2-octene	Conversion ^[b] [%]	<i>t</i> [h]
1	A	PPh ₃	135	94	1.3	1	> 99	15
	В		180	89	3	3	>99	12
2	Α	PCy₃	135	5	0	0	5	11
	В		180	80	4.2	9.8	>99	15
3	Α	$P(C_6F_5)_3$	135	3	0	0	7	15
	В		180	47	0	0	54	12
4	Α	P(<i>n</i> Bu)₃	135	trace			< 1 ^[c]	43
	В		180	8	0	0	17 ^[c]	24
5	Α	Na_2SO_3	135	trace			3	15
	B ^[d]		180	5	0	0	< 10	24
6	Α	H ₂ ^[e]	135	21 ^[f] (2 ^[f] +3)	1	0.8	35 (10)	15
	В		180	47 ^[f] (12 ^[f] + 1.2)	3.1	6	> 99 (35)	15
7	Α	3-pentanol	135	9	0	0	9	15
	B ^[d]		180	43	0	0	47	12
8	А	-	135	7	0	0	16	15
	В		180	50	0	0	>99	15
			_			/ N		

[a] Reaction conditions: 1,2-octanediol (0.5 mmol), **2** (0.01 mmol), reductant (0.55 mmol), PhCl (5 mL). [b] Determined by using GC with mesitylene (0.5 mmol) as an internal standard. [c] ¹H NMR spectroscopy conversion [d] Pentadecane was used as internal standard. [e] 40 bar H₂ pressure (parentheses results correspond to the reaction mixture in THF). [f] *n*-octane yield.

zene, 135 °C (Table 4). Linear aliphatic terminal diols were completely converted into the corresponding terminal olefins with high selectivities (entries 1-3). Decanediol and dodecanediol showed complete conversion after 40 h with a very low amount of internal olefin formation. Cis-cyclohexanediol was converted into cyclohexene in a low yield (10%), whereas the corresponding trans-cyclohexanediol did not show any reactivity (entries 4 and 5). This shows that the diol needs to be able to adopt a syn-configuration to be converted by the rhenium-based catalyst;^[8, 10, 13a] however, formation of the diolate intermediate from a cyclohexanediol substrate could be hampered by the steric

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Table 4. De	eoxydehydration of vicir	hal diols into olefins unde HO OH R R'	er optimised conditi + PPh ₃ 2 (2%) PhCl, 135 °C	ons catalysed by $2^{[a]}$ $_{R}$ $_{R'}$ + OPPh ₃ + H ₂ C)		
Entry	Substrate	Product	1-octene	Yield [%] ^[b] trans-2-octene	cis-2-octene	Conversion ^[b] [%]	<i>t</i> [h]
1	CH ₃ (CH ₂)5 OH	CH ₃ (CH ₂) ₅	94	1.3	1	>99	15
2		CH ₃ (CH ₂)7	90	3.7	3.5	>99	40
3		CH ₃ (CH ₂)9	94	1.4	1	86	40
4	ОН	\bigcirc	10			21	40
5	ОН	\bigcirc	trace			12	40
6	ОН		99			>99	40
7 ^[c]	OH OH	$\langle \rangle$	89			>99	40
8	OH OH		>99			>99	40
9	но он	$\langle \underline{\circ} \rangle$	49			>99	37
10	OH OH		17			29	38
[a] Reaction	conditions: 1,2-octane	diol (0.5 mmol), 2 (0.01 m	imol), PPh ₃ (0.55 mr	nol), PhCl (5 mL). [b] Det	termined by using GC	with mesitylene (0.5 m	imol) as

bulk of **2**. The aromatic vicinal diol phenyl-1,2-ethanediol produced an almost quantitative yield (99%) of styrene (entry 6), without polymerisation of the product, as was observed before by us for rhenium-mediated dehydrations towards styrenes.^[5] (*R*,*R*)-1,2-diphenyl-1,2-ethanediol selectively produced *trans*-stilbene in a quantitative yield (entry 8), whereas (*R*,*S*)-1,2-diphenyl-1,2-ethanediol (meso-hydrobenzoin) was fully converted into a mixture of *cis*-stilbene (89%) and *trans*-stilbene (10%) in 40 h.^[26] Moreover, 1,4-anhydroerythritol produced 49% 2,5- di-hydrofuran at full conversion (entry 9). Treatment of the internal aliphatic diol *syn*-4,5-octanediol gave a moderate conversion, resulting in only 17% *trans*-4-octene (entry 10). This observation could further indicate the sensitivity of **2** to the steric bulk of the substrate.

To probe the activity and stability of catalyst **2**, its loading was lowered to 0.05 mol% to convert 0.985 mmol 1,2-octanediol (0.144 g) at 180°C in 0.5 mL chlorobenzene. After 59 h, 86% conversion of 1,2-octanediol was achieved to yield 72% octenes as a mixture of 1-octene (62.5%) and 2-octenes (9.5%; *trans/cis* ratio = 1:2). The total turnover number for **2**, based on the amount of octenes formed, equalled 1400 per rhenium atom in the reaction. To the best of our knowledge, this turnover number for **2** is the highest reported to date for any of the published oxorhenium catalyst in a deoxydehydration reaction.

Finally, **2** was used in the deoxydehydration of two biobased polyols, that is, glycerol and erythritol. By using the optimised reaction conditions (vide supra), glycerol, which is the main side product from biodiesel production,^[27] was selectively converted to the corresponding olefinic product, allyl alcohol, in 91% yield at a substrate conversion of 94% in 26 h. In a similar reaction, by using 2.2 equiv. of PPh₃, erythritol was converted to 1,3-butadiene (**A**), with concomitant formation of partial deoxydehydration products 3-butene-1,2-diol (**B**), *cis*-2-butene-1,4-diol (**C**), and *trans*-2-butene-1,4-diol (**D**) (Scheme 3). As shown in Table 5, very poor conversion (20%) and yields were obtained in chlorobenzene at 140 °C over 26 h (entry 1). Upon increasing the reaction temperature of this heterogeneous mixture to 180 °C, complete conversion of erythritol produced 18% butadiene with **C** (5.8%) and **D** (2.2%) as side



Scheme 3. Conversion of (a) glycerol and (b) erythritol catalysed by 2.

Table 5.	Conversion of ery	thritol into	butadiene a	nd butene	diols cataly	sed by 2 . ^[a]		
Entry	Solvent	Т	Yield [%] ^{[b}				Conversion ^[b]	t
		[°C]	Α	В	C	D	[%]	[h]
1	PhCl	140	1.5	2.7	0.3	2.5	20	26
2	PhCl	180	18	-	5.8	2.2	>99	24
3	pyridine	180	30	4.3	3.0	4.9	60	15
4 ^[c]	3-octanol	170	67	-	-	-	>99	1.5

[a] Reaction conditions: Erythritol (0.5 mmol), **2** (0.01 mmol), PPh₃ (1.1 mmol), solvent (5 mL). [b] Determined by using GC with mesitylene (0.5 mmol) as an internal standard. [c] Erythritol (0.2 mmol), **2** (0.005 mmol), 3-octanol (0.67 mL); 7% 2,5-dihydrofuran and yields were determined by using ¹H NMR spectroscopy.

products (entry 2).^[28] Also, a homogeneous mixture in pyridine resulted in 30% butadiene with butene diols (B = 4.3%, C = 3%, and D = 4.9%) at 60% conversion of erythritol (entry 3).

Inspired by the work of Shiramizu et al.,^[12] who used MTO (2.5 mol%) as a catalyst in combination with 3-octanol as the reductant at 170 °C to convert erythritol into butadiene, we also used **2** as a catalyst under these conditions (Table 5, entry 4).^[29] This reaction produced 67% butadiene without the formation of by-products **B**–**D**, but with the formation of 7% 2,5-dihydrofuran (Scheme 4).



Scheme 4. Deoxydehydration of erythritol catalysed by using 2, with 3-octanol as the reductant.

Conclusions

We have shown efficient catalytic deoxydehydration reactions of vicinal diols to yield olefins by using the bulky Cp-based trioxorhenium catalyst 2. Different phosphine-based and conventional reductants were tested, including the least expensive reductant, molecular hydrogen. Under optimised reaction conditions, different types of vicinal diols are converted to their corresponding olefins, with limited isomerisation of the α -olefin products. The loading of 2 can be reduced to 0.05% to achieve a turnover number as high as 1400 per rhenium. These data point at the combined activity and stability of 2 in deoxydehydration reactions, and render 2 a promising lead for the further development of Cp-based trioxorhenium catalysts, as envisioned by Gable et al. $^{\scriptscriptstyle [15a]}$ Preliminary experiments show that ${\bf 2}$ may serve as a powerful catalyst for the conversion of biobased polyols to olefins. The further development of Cp-based trioxorhenium catalysts for the improved conversion of polyols and sugars into olefins, and mechanistic studies of such catalyst systems, are on-going.

Experimental Section

General: All chemicals, including solvents, were degassed by using either the freeze-pump-thaw method or degasification under

vacuum. Toluene, THF, and acetonitrile solvents were obtained from a MBraun MB SPS-800 system, and degassed. Triphenylphosphine was crystallised in ethanol and dried under vacuum. Unless otherwise stated, all other commercial chemicals were used without further purification. NMR spectra were recorded on a Varian VNMRS400 (400 MHz) instrument at 298 K.

IR spectra were recorded by using a PerkinElmer Spectrum One FTIR

spectrometer in the range of 650–4000 $\rm cm^{-1}.$ ESI-MS spectra were recorded by using a Waters LCT Premier XE instrument.

Synthesis of 1: In a dried Schlenk tube, Re₂(CO)₁₀ (1.0 g, 1.5 mmol) was charged and degassed under vacuum for 30 min, and an excess of 1,2,4-tri(tert-butyl)cyclopentadiene (1 mL, 2 mmol) was added under a nitrogen atmosphere. The resulting mixture was refluxed at 150°C for 30 min. At regular time intervals, the reaction temperature was increased to reach 210°C in 4 h. The reaction mixture was maintained at 210°C for 30-45 min to allow for the complete conversion of the rhenium starting material. After cooling to ambient temperature, a sample of the solidified reaction mixture was obtained for thin layer chromatography, which showed complete conversion of the rhenium starting material. After removing the excess tri(tert-butyl)cyclopentadiene by washing with cold hexane and drying under vacuum, 1 was obtained as a bright white solid in 42% yield. Crystals of 1, suitable for single XRD, were obtained at -30° C from a solution in a 2:1 (1.5:0.75 mL) solvent mixture of dichloromethane/hexane. ¹H NMR spectroscopy (400 MHz), CDCl₃ (7.26 ppm): $\delta = 1.19$ (s, 9H, tBu), 1.37 (s, 18H, tBu), and 5.35 ppm (s, 2H, Cp-H). ¹³C NMR spectroscopy (400 MHz), CDCl₃ (77.16 ppm): δ = 30.94, 32.21, 33.09, 34.51, 85.74, 113.52, 115.73, and 196.61 ppm. IR [attenuated total reflectance (ATR)/FTIR]: $\tilde{\nu} = 1247$, 1365, 1463, 1485, 1886, 1900, 2004, 2872, and 2965 cm $^{-1}$; ESI-MS: calcd for $[C_{20}H_{29}ReO_3]^+\!=\!504.1675;$ found = 504.1729; elemental analysis calcd (%) for $C_{20}H_{29}ReO_3$ (504. 17): C 47.70, H 5.80, O 9.53, and Re 36.97; found: C 45.42, H 9.11, O 11.26, and Re 34.21.

Synthesis of 2: Tricarbonyl complex 1 (1 g, 1.98 mmol) was degassed in a dried Schlenk tube by stirring for 30 min under vacuum, followed by the addition of degassed benzene (50 mL), and H₂O₂ (35% in water, 5 mL, 31 equiv.) mixed with concentrated H₂SO₄ solution (0.1 mL). The resulting mixture was refluxed for 15 h at 80°C, after which the yellow organic layer was separated from the water layer by extracting with benzene $(3 \times 25 \text{ mL})$ in open air. Then, the organic layer was washed with demineralised water (2 \times 100 mL), 5% NaHCO₃ solution (1 \times 100 mL), and brine solution (1 \times 100 mL), before it was dried over Na₂SO₄. After the removal of benzene in vacuo, 2 was obtained as a bright yellow crystalline compound in 77% yield, and was further purified by column chromatography with dichloromethane and hexane (1:1) as the eluent (yield = 73%). Crystals of 2 were obtained from a 2:1 mixture of dichloromethane/hexane (1/0.5 mL) at -30 °C. ¹H NMR spectroscopy, CDCl₃ (7.26 ppm): $\delta =$ 1.41 (s, 9H, tBu), 1.55 (s, 18H, tBu), 6.55 ppm (s, 2H, Cp–H); ¹³C NMR spectroscopy, CDCl₃ (77.16 ppm): $\delta = 30.11$, 32.30, 33.29, 35.18, 110.93, 134.71, and 136.19 ppm. IR (ATR/FTIR): $\tilde{v} = 832$, 877, 917, 1236, 1369, 1462, 2967 cm⁻¹; ESI-MS: calcd for $\label{eq:constraint} [C_{13}H_{29}ReO_3 + H]^+ = 469.1683; \quad found = 469. \quad 1753; \quad calcd \quad for$ $[C_{13}H_{29}ReO_3 + Na + CH_3CN]^+ = 532.1832$; found = 532.1820; elemen-

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tal analysis calcd (%) for $C_{17}H_{29}ReO_3$ (468.17): C 43.66, H 6.25, O 10.26, Re 39.82; found: C 43.23, H 6.41, O 10.27, Re 39.49.

General procedure for catalytic deoxydehydration: Unless otherwise noted, all reaction mixtures were prepared inside a glove box under a nitrogen atmosphere or on a conventional Schlenk line in a 15 mL thick-walled glass pressure tube (Ace) fitted with a Teflon screw-cap. 1,2-octanediol (0.5 mmol), 2 (0.01 mmol), and mesitylene (0.5 mmol) were dissolved in chlorobenzene (5 mL) and mixed well. Finally, PPh₃ (0.55 mmol) was added in the reaction mixture to avoid over-reduction of 2. Alternatively, stock solutions were prepared in chlorobenzene. Then, the closed reaction vessel was brought into a preheated silicone oil bath at 135 or 180 °C. After the reaction, aliquots of the reaction mixture were diluted with acetone (for olefins) or ethylacetate (for diols). GC measurements were performed by using a PerkinElmer Autosystem XL gas chromatograph equipped with a PerkinElmer Elite-17 column (length = 30 m, internal diameter = 0.32 mm, film thickness = 0.50 μ m), and with a flame ionisation detector. GC method: 40°C, 5 min; 3°Cmin⁻¹ to 55°C; 20°Cmin⁻¹ to 250°C; 250°C, 10 min. All olefinic products were known compounds and were calibrated against mesitylene for quantification.

Typical procedure for deoxydehydration with hydrogen as the reductant: Diol (1 mmol), 2 (0.02 mmol), and mesitylene (1 mmol) were mixed with 10 mL of chlorobenzene or THF in an autoclave vessel. The solution was flushed three times with 40 bar H₂ pressure and then heated to the aforementioned temperature. Samples were taken for GC and GC-MS after cooling in an ice bath.

Typical procedure for polyol conversion: Polyol (0.5 mmol), 2 (0.01 mmol), mesitylene (0.5 mmol), and PPh₃ (0.55 or 1.1 mmol) were weighed directly into the reaction tube, and the solvent (5 mL) was added. The reaction tube was closed and heated in a preheated oil bath. The mixture was cooled in an ice bath and homogenised with pyridine. Samples were taken directly by syringe to analyse for volatiles. Then, the mixture was further diluted in pyridine to homogenise the mixture for diol and polyol analysis. Further, acetylation was performed with acetic anhydride (0.5 mL sample, 1 mL pyridine, 0.3 mL acetic anhydride) at 70 °C for 20-30 min to determine the amount of unreacted glycerol. When 3-octanol was used as the reductant, the catalyst (0.03 mmol) was dissolved in 3-octanol (4 mL). 0.67 mL of this stock solution was added to the reaction tube in which erythritol (0.2 mmol) was already weighed. After the reaction, the tube was cooled in an ice bath and 20 µmol mesitylene was added. After mixing, 0.1 mL of the mixture was diluted in CDCl₃. Yields from ¹H NMR spectroscopy were calculated based on the aromatic proton signals of mesitylene.

X-ray crystal structure determinations: X-ray reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073$ Å). The intensities were integrated with the Saint software.^[30] Absorption correction and scaling based on multiple reflections were performed with the SADABS software.^[31] The structure of 1 was solved with the DIRDIF-08 software,^[32] and the structure of **2** was determined by using the SIR-97 software.[33] Least-squares refinement was performed with the SHELXL-97 software against F² of all reflections.^[34] Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were located in difference Fourier maps. The ring hydrogen atoms H3 and H5 in 1 were refined freely by using isotropic displacement parameters; all other hydrogen atoms were refined with a riding model. Geometry calcu-

lations and higher symmetry checking was performed with the PLATON program.[35]

CCDC 929019 (1) and CCDC 929020 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 1: $C_{20}H_{29}O_3Re$, formula weight (F_w) = 503.63, colourless block, $0.24 \times 0.22 \times 0.18$ mm³, monoclinic, space group = $P2_1/c$ (no. 14), unit cell dimensions: a = 10.6140(4), b = 11.5980(5), and c =16.7925(7) Å, angle: $\beta = 97.0861(13)^{\circ}$, unit cell volume V =2051.39(15) Å³, number of formula units per unit cell Z=4, density calculated from the crystal cell and content $D_x = 1.631 \text{ g cm}^{-3}$, linear absorption coefficient $\mu = 5.94 \text{ mm}^{-1}$. 35746 reflections were measured at a temperature of 150(2) K up to a resolution of (sin θ / λ)_{max} = 0.65 Å⁻¹, and 4682 reflections were unique (R_{int} = 0.017), of which 4327 were observed [$l > 2\sigma(l)$]. 234 parameters were refined with no restraints. R1/wR2 [I>20(I)]=0.0118:0.0282, R1/wR2 [all reflections] = 0.0140:0.0290, and S = 1.028. Residual electron density between -0.36 and $-0.64 \text{ e} \text{ Å}^3$.

Compound 2: $C_{17}H_{29}O_{3}Re$, $F_{w} = 467.60$, yellow needles, $0.40 \times 0.24 \times$ 0.14 mm³, monoclinic, space group = $P2_1$ (no. 4), unit cell dimensions: a = 8.6569(8), b = 11.3605(11), and c = 9.2162(8) Å, angle: $\beta =$ 108.164(2)°, $V = 861.22(14) \text{ Å}^3$, Z = 2, $D_x = 1.803 \text{ g cm}^{-3}$, $\mu =$ 7.06 mm⁻¹. 18827 reflections were measured at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}\!=\!0.65~\text{\AA}^{-1}\!.$ 3900 reflections were unique ($R_{\rm int} = 0.023$), of which 3864 were observed [l > $2\sigma(l)$]. 200 parameters were refined with one restraint (floating origin). R1/wR2 [$l > 2\sigma(l)$] = 0.0093:0.0234, R1/wR2 [all reflections] = 0.0095:0.0234, and S = 1.099. Flack parameter: x = 0.007(4).^[36] Residual electron density between -0.44 and $0.22 \text{ e} \text{ Å}^3$.

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