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Rhodium Hydroformylation Catalysts | *Very Important Paper* |

Water-Soluble, Disulfonated alpha-Diimine Rhodium(I) Complexes: Synthesis, Characterisation and Application as Catalyst Precursors in the Hydroformylation of 1-Octene

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Abstract: The synthesis and characterisation of two new water-soluble Rh^{I} mononuclear 1,4-diazabutadiene (DAD^{s}) complexes of general formula: [Rh(DAD^{s}-R)(COD)], where (DAD^{s} = sulfonated-tagged–1,4-diazabutadiene, COD = cyclooctadiene; and R = H or $C_{10}H_8$), are described. The rhodium(I) complexes were obtained via a complexation reaction of $[Rh(COD)(MeCN)_2]BF_4$ with the sulfonated α-diimine (DAD) ligands, which were previously obtained from a Schiff base condensation reaction of 4-aminophenol with either 1,2-ethanedione or acenapthenequinone. All rhodium complexes and their precursor ligands were characterised using ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopy and mass spectrometry. Their performance as catalyst precursors in the hydroformylation of 1-octene was assessed and compared to those of the non-sulfonated Rh^{I} mononuclear 1,4-diazabutadiene (DAD) complexes. Utilisation of the water soluble [Rh(DAD^{s}-R)(COD)] lead to high conversions and regioselectivity (linear/branched aldehyde ratio) in the aqueous biphasic hydroformylation of 1-octene. Additionally, the catalysts were recovered by phase separation and are reusable over four consecutive catalytic runs without significant loss in catalytic activity.

Introduction

The contribution of catalysis to economic development and environmental sustainability cannot be over-emphasised and this is due to the high activity and selectivity of catalysts to the desired product.[1–3] In the industrial chemical sector, 85 % of most organic transformations use various transition metal based catalysts.[4] Rhodium-catalysed reactions such as hydroformylation convert olefins to aldehydes that are useful intermediates to synthesise pharmaceuticals,[5] fine chemicals,[6] and agrochemicals.[7] This transformation proceeds favourably using homogeneous catalysts and over the years significant progress has been achieved for these catalysed reactions.[8] Despite these improvements, the challenges of the homogeneous catalysis is the difficulty of recovery and recyclability or reuse of these expensive metal catalysts.[9,10] One strategy that has been established to address these challenges is the use of aqueous phase catalytic systems which immobilise metal complexes in water, used as the reaction medium.[11–16] The Rührchemie/Rhône Poulenc "Oxo" process is a well-established industrial application which exemplifies aqueous biphasic catalysis utilizing a water soluble rhodium complex based on the trisodium salt of tris(*m*-sulfonatophenyl)phosphine (TPPTS) ligand. However, TPPTS based ligands are highly unstable in the presence of air/oxygen and this process is limited to only short chain olefins (< C4).[13,17] The development of new water-soluble catalysts is thus an important and ongoing research activity at both academic/industrial levels and a significant advancement is been made to improve aqueous-phase hydroformylation reactions.[18,12] The underlying idea is to introduce hydrophilic substituents into sterically demanding and electron-rich ligands that display high catalytic activity in conventional organic solvents. In our previous work, we have reported on Rh^{I} complexes bearing Schiff base ligands containing *N,O*- and *N,P*-chelates.[19–22] These catalyst precursors are highly active and chemo- and regioselective in the hydroformylation of 1-octene.

In aqueous reactions, the catalyst precursor is dissolved in water and the substrate is contained in the organic phase, forming two layers (biphasic). Upon heating, there is an interfacial interaction between the catalyst and the substrate and on cooling the phases separate. The water-soluble catalyst is easily separated from the product mixture by simple decantation as shown in Figure 1. This biphasic method allows for catalyst recovery, possible multiple recycling and high product turnover. This strategy correlates well with Green Chemistry principles in the use of water as a solvent and minimising leaching which in turn promotes environmental conservation and sustainability.[23,24]

Following our previous studies, we were interested in the α-diimine (1,4-diazabutadiene skeleton) ligand scaffold, which has been used in catalytic reactions such as olefin polymerisation[25–27] and C–C cross-coupling reactions because of their versatile coordination behaviour and the interesting properties of their metal complexes.[28,29] The two key features of α-diimine ligands are: (i) the presence of two *exo* imines to the two

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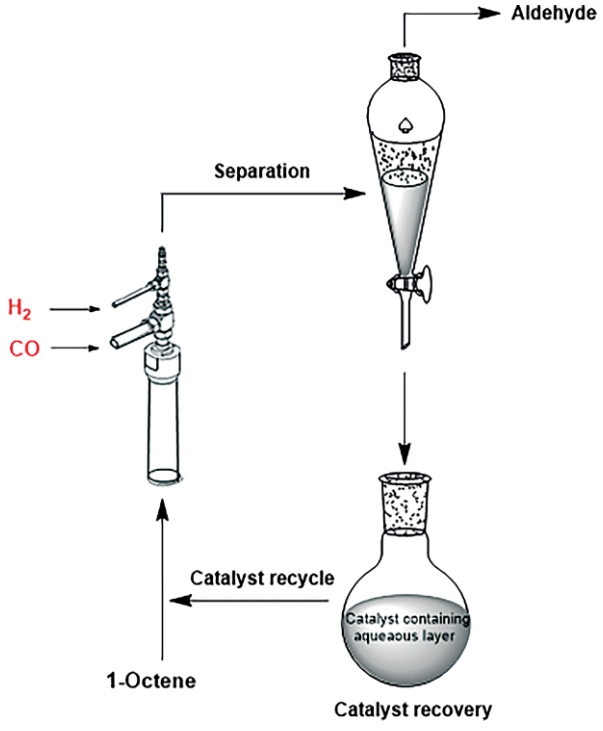


Figure 1. Strategy to recycle and reuse a water-soluble metal precatalyst.

alpha carbons system which leads to better σ-donating and better π-accepting properties,[30–32] and (ii) the stereoelectronics of the substituents bonded to the imine.[33] Extensive chemistry has been carried out with similar imine systems such the 2,2′-bipyridine and phenanthroline. These are under-explored and the simplest representative of this class of compounds (1,4-disubstituted, 1,4-diaza1,3-butadienes) have been reported to have a flexible N=C–C=N skeleton and unusual electron donor and π-accepting properties.[34] In this study, we chose α-diimine ligands as model compounds with *para* hydroxyl groups at the focal point which allows for the attachment of water-soluble entities and varied the backbone which impacts on the steric and electronic properties.

To the best of our knowledge, hydroformylation involving disulfonated α-diimine rhodium(I) complexes has not been explored. Herein, we report the synthesis of water-soluble Rh^{I} precatalysts bearing sulfonated *N,N-bis(arylimino)ethane* and sulfonated α-diimine ligands of the type *N,N- bis(arylimino)-acenaphthene* (aryl-BIAN) for the hydroformylation reaction of 1-octene in an aqueous medium.

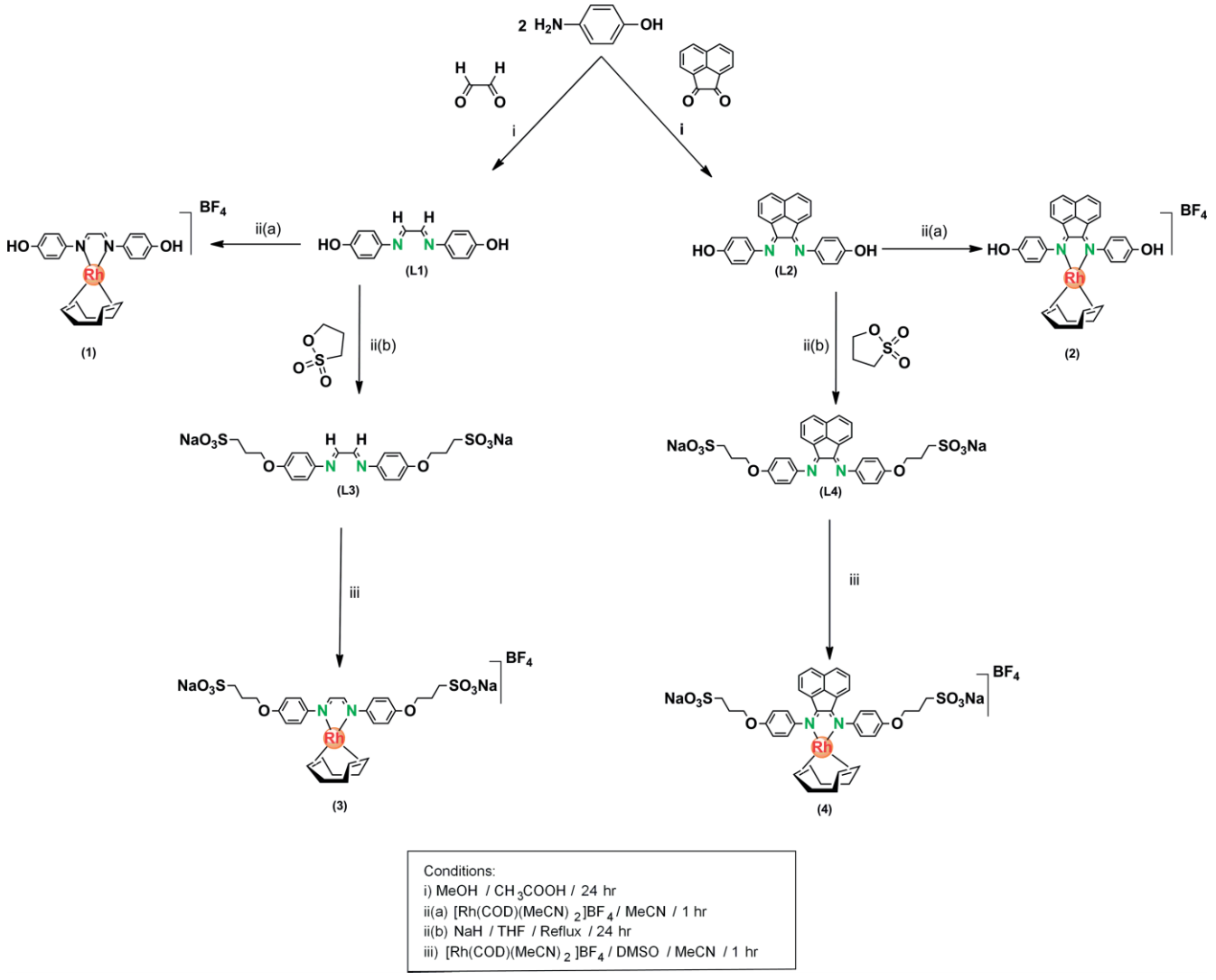
Results and Discussion

Synthesis and Characterisation of Ligands and Rhodium(I) Catalyst Precursors

The alpha-diimine ligands **L1** and **L2** were synthesised via a Schiff base condensation reaction of the carbonyl compounds (1,2-ethanedione and acenapthenequinone) with two molar equivalents of 4-amino phenol in methanol and using a catalytic amount of acetic acid (Scheme 1). The peak associated with the primary amine of 4-aminophenol is absent in the ^{1}H NMR spectrum of ligand **L1** and **L2** confirming a successful Schiff base condensation reaction had occurred. All the expected peaks of aromatic protons were observed in ligand **L1** and **L2** between 6.92 ppm and 9.40 ppm respectively. Notably, the peak for phenolic protons of ligand **L1** and **L2** appears as a broad singlet at δ = 9.78 ppm and δ = 9.40 ppm respectively. The signal for the phenyl protons in ligand **L2** appears as a singlet due to the symmetrical nature of the molecule as a result of the rigid acenaphthene backbone which prevents rotation around the imine carbon–carbon bond and forces the imine nitrogen atoms to remain in a fixed orientation.[35,36] It has been reported that *bis(N-arylimino)acenaphthene* derivatives of alpha diamine ligands are more rigid and sterically bulky compared to diimine ligands derived from glyoxal or acyclic diketones and this rigidity may impose stable chelation to metal complexes exhibiting a more limited range of bonding modes and impacting high chemical stability with respect to hydrolysis and cleaving of the central C–C bond.[37–39] The IR spectra of **L1** and **L2** show absorption bands for the imine C=N bond at 1603 cm^{-1} and 1659 cm^{-1} and the O–H bond at 3075 cm^{-1} and 3289 cm^{-1} respectively.

The alkylation of the hydroxy group in ligand **L1** and **L2** was performed in dry tetrahydrofuran using 1,3-propanesultone for the introduction of the alkyl-sulfonate group (Scheme 1). Initially, the phenoxide was generated using the deprotonating agent NaH, followed by ring-opening of the cyclic sulfonate (1,3-propanesultone) via nucleophilic attack from the phenoxide species which occurs with cleaving of the C=O.[40,41] The modification occurred in high yield (82 %) when these reagents were added in slight excess. The absence of hydroxyl proton signal in the ^{1}H NMR spectra of ligands **L3** and **L4** respectively confirms the successful deprotonation or formation of a phenoxide species. The phenyl protons attached to the imine appear as quartet signals alluding to the fluxionality resulting from a change from a symmetrical to asymmetrical molecule upon sulfonation. Both ligands display excellent solubility in water and DMSO at room temperature.

Complexation was achieved using $[Rh(COD)(MeCN)_2]BF_4$, prepared *in situ* from $[(Rh(COD)Cl)_2]$ and $AgBF_4$ in acetonitrile at room temperature. The water-soluble rhodium(I) complexes **3** and **4** were obtained in quantitative yield upon reaction of $[Rh(COD)(MeCN)_2]BF_4$ with the appropriate ligand at room temperature. DMSO proved useful as the solvent of choice as it possesses sufficient polarity to dissolve the salt-like ligands and complexes. The displacement of acetonitrile from $[Rh(COD)(MeCN)_2]BF_4$ with the α-diimine ligands was facile, affording new rhodium cationic complexes. The hydrophilic complexes were simply purified by washing the product mixture with acetone to remove any unreacted $[Rh(COD)(MeCN)_2]BF_4$. The ^{1}H NMR spectrum of the metal complexes show signals consistent with the proposed structure. Comparing the ^{1}H NMR spectrum of ligand **L4** and complex **4**, a significant down field shift was observed for the acenaphthene ring proton upon coordination caused by increase in electron density. However, the protons of the phenyl bonded to the imine are observed as two doublets which may be attributed to the coordination of the



Scheme 1. Synthesis of Rh^{I} catalyst precursors **1**–**4**.

imine nitrogen to the Rh metal centre. The signals for the cyclooctadienyl entities are observed as broad signals each peak integrating for 4 protons. The ^{1}H NMR spectrum for complex **3** shows trends similar to those observed in the NMR spectrum of complex **4**. The protons of the cyclooctadienyl entities are observed in complex **3** as a singlet and multiplets at 3.92 ppm, 2.35 ppm and 1.72 ppm. Coordination-induced down field shift was observed for the imine proton H-1 from 8.44 ppm to 8.68 ppm. The absorption bands of the imine functionality in the infrared spectra of the Rh^{I}-COD complexes (**3** and **4**) decrease on coordination of the metal compared to that observed in the metal-free ligands. This is due to the degree of back bonding from the metal into the π^* (antibonding) orbitals of the imine (synergic effect). The non-sulfonated α-diimine rhodium complexes (**1** and **2**) used in this study were readily synthesised by reacting the ligands either **L1** or **L2** with $[Rh(COD)(MeCN)_2]BF_4$ in acetonitrile (Scheme 1). The ^{1}H NMR spectra of complex **1** and **2** display all the expected aromatic and COD signals.

Preliminary Screening Using Catalyst Precursor 1 in the Hydroformylation of 1-Octene

Catalyst precursor complex **1** (where R = H) being the simplest and most representative structure of all the precatalysts synthesised was used for optimisation experiments. The hydroformylation reaction was attempted by varying the temperature (55 °C, 75 °C and 95 °C) and syngas pressure (20 bar, 30 bar and 40 bar). All the reactions were performed for 4 hours in toluene (5 mL) and the products were analysed using gas chromatography with *n*-decane as the internal standard.

Under conditions of 55 °C and 20 bar, minimal conversion of 1-octene was observed and increasing the temperature to 75 °C at the same pressure resulted in an increase conversion of 1-octene with the formation of more isooctenes. This is because an increase in temperature leads to more alkene activation.[42] However, at much higher temperature of 95 °C at the same pressure (20 bar) the isomerisation of 1-octene was greatly reduced, and an overall increase in conversion to aldehydes was

observed. This might be attributed to the increased solubility of the catalyst at higher temperatures thereby leading to higher isomerisation and subsequent hydroformylation of 1-octene. Generally, with respect to substrate conversion, an increase in temperature leads to increased catalyst activity. At constant temperature and increasing pressure (20, 30 and 40 bar), a general increase in the turnover frequency conversion of 1-octene to aldehydes and lower formation of isooctene was observed. It has been reported that increasing the CO pressure in hydroformylation results in the increase of CO concentration in the reaction medium and scavenges the vacant site of the 16-electron alkyl rhodium species reducing isomerisation and accelerating the CO migration step.[43] This ideally, results in a higher conversion rate of the olefin to aldehydes. However, under these conditions, the gradual reduction of linear aldehydes was observed and a considerable amount of branched aldehydes is formed. This is indicated by the decrease in *n:iso* ratio. Optimum temperature and pressure conditions were established at 75 °C and 40 bar and further used for catalyst comparison with respect to conversion, *n:iso* ratio and turnover frequency.

Hydroformylation Reaction Using Catalyst Precursors 3–4 in the Aqueous Phase

The water-soluble 1,4-diazabutadiene (DAD^s) rhodium(I) complexes (**3** and **4**) were used as catalyst precursors under the established optimum condition (75 °C / 40 bar) in water (5 mL) and compared to the non-sulfonated 1,4-diazabutadiene rhodium(I) complexes (**1** and **2**).

All catalyst precursors gave high conversions (Table 1) greater than 95 % and showed good regioselectivity for linear aldehydes (> 65 %). Complexes **3** and **4** showed high conversions and turnover frequencies in comparison with complexes **1** and **2**, in favour of aldehydes (> 85 %) of which > 65 % is nonanal. The excellent solubility in water can, in part, account for the better activity as there is more substrate to catalyst interaction upon increase in temperature. The percentage conversion of the water-soluble Rh^I complexes (**3** and **4**) were also evaluated at various times (Figure 2); this was conducted using the optimised conditions 75 °C and 40 bar. The precursors were evaluated at intervals of 1 hour, 2 hours, 4 hours, 6 hours and 8 hours. In general, near-quantitative conversions of 1-octene (> 99 %) was observed after 6 hours and slight differences in catalytic rates are seen in the first 2 hours.

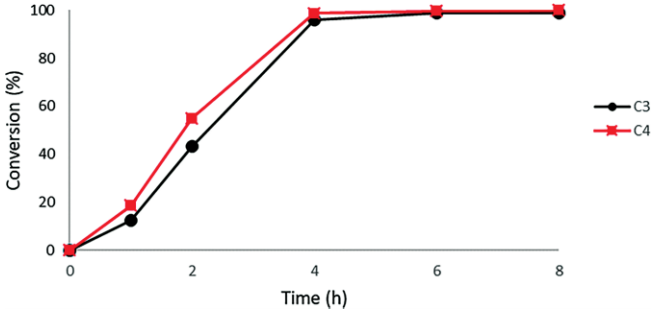


Figure 2. Percentage conversion of 1-octene over 8 hours using catalyst precursors (**3** and **4**). Reactions performed at 75 °C and 40 bars.

Recyclability of Catalyst Precursors 3 and 4

The recyclability studies over four catalytic runs was performed as follows. After a hydroformylation reaction, the reaction mixture was cooled to room temperature and the product (contained in the organic phase) was separated by decantation and the catalyst-containing solution (aqueous phase) was reused over three consecutive cycle by introducing the fresh substrate. Overall conversions greater than 65 % was observed over four cycles, with the first two cycles showing conversions greater than 90 % with high regioselectivity towards linear aldehydes (Figure 3).

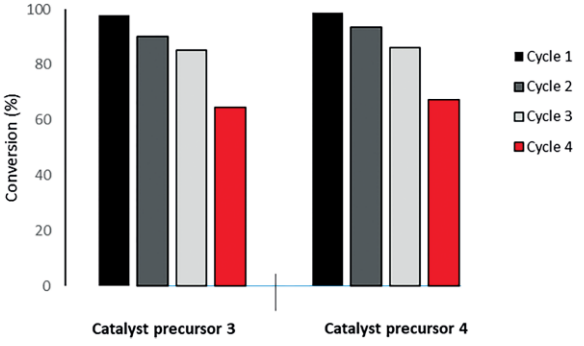


Figure 3. Recyclability of catalyst precursors **3** and **4** in the hydroformylation of 1-octene.

The regioselectivity of each catalyst varied upon recycling as shown in Figure 4. This may be attributed to changes in the structure of the active catalyst under hydroformylation conditions as it is recycled. Despite this, a significant drop in conversion and turn over frequencies was observed after the third cycle for both catalyst precursors **3** and **4** with an increase in the formation of isooctenes. In all experiments, noticeable catalyst decomposition was observed by the darkened colouration of the aqueous phase. Also, the dark colour intensity increased after each cycle and the efficiency of the catalyst (**3** and **4**) upon recycling dramatically decreased (< 65 % conversion). With respect to regioselectivity, increased formation of linear aldehydes was observed using catalyst precursor **4**. It has been reported that the *n/iso* ratio of the product depends mainly on steric effects which favours anti-Markovnikov addition making the catalyst more selective towards the formation of the linear aldehyde.[44]

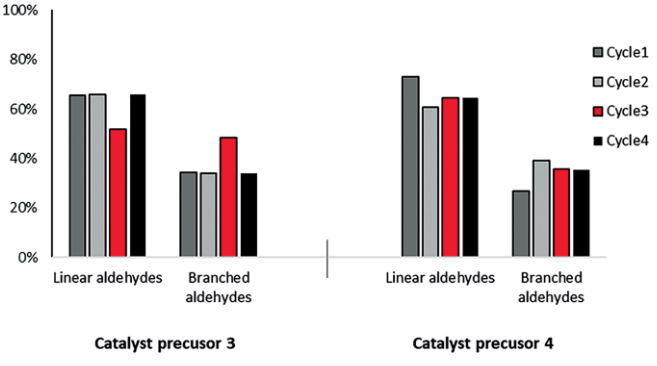


Figure 4. Regioselectivity of catalyst precursors **3** and **4** in the hydroformylation of 1-octene.

Table 1. Hydroformylation of 1-octene using catalyst precursors **1**–**4**.[a]

Entry	Precatalyst	Conversion [%]	Aldehydes [%]	Linear aldehydes [%]	Branched aldehydes [%]	Iso-octenes [%]	*n*:iso	TOF [h^{-1}]
1	**1**	95	72	69	31	28	2.21	329
2	**2**	97	70	70	30	30	2.36	317
3	**3**	98	86	66	34	15	1.91	522
4	**4**	99	88	73	27	12	2.73	539
5	**1**+Hg	54	41	63	37	59	1.72.	142
6	**2**+Hg	56	38	61	29	60	2.14	206
7	**3**+Hg	98	86	64	34	14	1.90	566
8	**4**+Hg	98	88	74	26	13	2.70	556

[a] Reaction conditions: The reactor (90 mL) was loaded with toluene (5 mL) for catalyst precursors **1** and **2**, or H_2O (5 mL) for catalyst precursors **3** and **4**, 1-octene (0.805 g, 6.37 mmol), internal standard *n*-decane (0.204 g, 1.435 mmol) and Rh–metal loading (2.87×10^{-3} mmol). The reactor was purged with nitrogen three times, followed by purging three times with syngas. Catalyst to substrate ratio used was (1:2500). The reactions were carried out for 4 hours at 75 °C/40 bar and the data was analysed using GC-FID. TOF = (mmol of aldehydes/mmol of Rh)/time. Average error estimate: (**1**) = ±0.14, (**2**) = ±0.11, (**3**) = ±0.18, (**4**) = ±0.10.

Inductively Coupled Plasma Spectrometry Studies

To investigate the origin of this decrease in catalytic performance, the recycled organic layer was analysed using ICP-MS analysis. The data showed lower amounts of rhodium concentration in the organic layer in first cycle and negligible leaching was observed in the second cycle (less than < 0.003 %) and no rhodium leaching in the third and fourth cycle suggesting no significant decrease of rhodium concentration in the aqueous phase. However, the decrease efficiency of the catalyst after the second cycle may be due to the degradation of the catalyst upon further recycling thereby suggesting a decrease in the formation of the active rhodium species in the reaction medium. This phenomenon is consistent with catalyst decomposition.

Mercury Poisoning Experiments

A mercury poisoning test was used to determine the heterogeneity of a catalytic process and it is based on the ability of mercury to combine with metals or to get adsorbed unto their surface. This therefore establishes if a catalyst acts as a molecular species or is heterogeneous in nature (nanoparticles) as mercury is believed to only interact with heterogeneous catalysts forming amalgam and has no influence on molecular catalysts. The mercury poisoning test was performed by adding a drop of mercury into each reactor containing catalyst precursor using the temperature (75 °C), time (4 hours) and pressure (40 bar) (Table 1, entries 5–8). A substantial drop in conversion is observed for the non-water-soluble rhodium precatalysts **1** and **2** in the presence of mercury suggesting a combination of homogeneous and heterogeneous catalysis while no significant changes in conversion was observed with the water-soluble analogues (**3** and **4**) in the presence of mercury. This suggests that the water-soluble precatalysts act as homogeneous molecular precatalysts in solution.

Conclusion

In summary, two new water-soluble disulfonated α-diimine ligands and their corresponding rhodium complexes were synthesised and fully characterised using various spectroscopic and analytical techniques. The complexes are highly soluble in water at room temperature, and the efficiency of the complexes was evaluated as catalyst precursors in the aqueous hydroformylation of 1-octene and compared to those of their non water-soluble analogues. Excellent conversion of 1-octene to aldehydes with higher turnover frequencies and chemo- and regioselectivities were observed using catalyst precursors **3** and **4**. The recyclability tests revealed that the water-soluble precatalysts can be reused up to four times with a loss in catalytic activity observed after the third cycle. The mercury drop test confirmed the molecular nature of the water-soluble precatalysts and the absence of any nanoparticles. Further *in situ* temperature-programmed decomposition (TPD) studies under controlled conditions are required to fully establish the stability of these complexes.

Experimental Section

General: All solvents were purchased and purified according to standard methods. All reagents were purchased from Merck and used without further purification. 1,2-bis(4-hydroxylphenylimino) glyoxal,[45] **L1**[46] and **L2**[47] were synthesised according to modified, previously reported methods. Nuclear Magnetic Resonance (NMR) spectra were recorded on either a Bruker Ultrashield 400 Plus (^{1}H: 400.22 MHz; ^{13}C: 100.65 MHz) or a Bruker 300 MHz (^{1}H: 300.08 MHz; ^{13}C: 75.46 MHz) spectrometer at ambient temperature. ^{1}H and ^{13}C NMR chemical shifts are referenced to the deuterated solvent. Infrared (IR) spectra were determined using a Perkin–Elmer Spectrum 100 FT-IR spectrometer, and were recorded using Attenuated Total Reflectance Infrared spectroscopy (ATR-IR). Melting points were determined using a Büchi melting point apparatus B-540. Mass spectrometry was carried out using a Waters API Quattro Micro Triple Quadrupole electrospray ionisation mass spectrometer. Hydroformylation samples were analysed on a Perkin Elmer Clarus 580 gas chromatography. Inductively coupled plasma emission spectroscopy experiments were carried out using Thermo-Fisher X-Series II quadrupole ICP-MS.

Synthesis of Disulfonated α-Diimine Ligands: *Synthesis of L3*: Sodium hydride (0.033 g, 1.37 mmol) dispersed in mineral oil was suspended in 10 mL of dry THF, in a two-neck flask. A solution of **L1** (0.100 g, 0.420 mmol) dissolved in dry THF (2 mL) was added.

The mixture was allowed to stir under argon for one hour at room temperature and then 1,3-propanesultone (0.15 g, 1.23 mmol) in dry THF (2 mL) was added and allowed to stir for 8 h under reflux at 50 °C. The reaction mixture turned orange. After cooling to room temperature, a precipitate was collected by suction filtration, and washed with THF and acetone to remove the unreacted excess sultone. The product was purified by precipitation from DMSO/acetone mixture and dried under vacuum for 8 h. **L3** was isolated as an orange powder. Yield: 0.180 g, (82 %). M.p: 229–230 °C. ^{1}H NMR (300 MHz, D_2O-d_2) (ppm) = 7.96 (s, 2H, N=C-H), 7.25 (d, 4H, ^3J = 8.80 Hz Ar-H), 6.93 (t, 4H, ^3J = 7.20 Hz Ar-H) 3.99 (t, 4 H, ^3J = 8.30 Hz O-CH_2), 2.98 (t, 4H, ^3J = 7.40 Hz CH_2-SO_3), 2.12 (m, 4 H, CH_2-CH_2-CH_2). ^{13}C NMR (151 MHz, [D_6]DMSO) δ = 159.25, 157.93, 143.09, 123.56, 115.73, 67.69, 48.39, 25.80. FT-IR (ATR, cm^{-1}) ν = 1185 and 1054 (O=S=O). HR-ESI-MS (*m/z*) = 526.9700 [M + H]$^+$.

Synthesis of L4: Sodium hydride (0.015 g, 0.700 mmol) dispersed in mineral oil was suspended in 10 mL of dry THF, in a two-neck flask. A solution of **L2** (0.100 g, 0.270 mmol) dissolved in dry THF (2 mL) was added. The mixture was allowed to stir under argon for one hour at room temperature and then 1,3-propanesultone (0.08 g, 0.65 mmol) in dry THF (2 mL) is added and allowed to stir for 8 h under reflux at 40 °C. The reaction mixture turned dark red. After cooling to room temperature, the precipitate was collected by suction filtration and washed with THF and acetone to remove the unreacted excess sultone. The product was purified by recrystallisation using a water/ethanol mixture and dried under vacuum for 8 h. **L4** was isolated as a red powder. Yield: 0.122 g, 67 %. M.p: 154 –156 °C. ^{1}H NMR (300 MHz, [D_6]DMSO): δ (ppm) = 8.08 (d, 2H, ^3J = 7.9 Hz, ArH), 7.57 (t, 2H, ArH), 6.96 (d, 2H, ^3J = 7.2 Hz ArH), 7.05 (dd, 8H, ArH), 4.15 (t, 4 H, ^3J = 6.5 Hz OCH_2), 2.63 (t, 4H, CH_2-SO_3), 2.09 (m, 4 H, $CH_2CH_2CH_2$). ^{13}C NMR (151 MHz, [D_6]DMSO) δ = 179.32, 161.60, 157.26, 124.29, 120.60, 116.88, 68.35, 49.46. FT-IR (ATR, cm^{-1}) ν = 1181 and 1036 (O=S=O). HR-ESI-MS (*m/z*) = 653.0217 ([M + H]$^+$, 65 %).

Synthesis of Rhodium(I) Complexes

Rhodium(I) Complex 1: A mixture of silver tetrafluoroborate (0.243 g, 1.25 mmol) and [Rh(COD)Cl]$_2$ (0.308 g, 0.624 mmol) was stirred in acetonitrile (10 mL) for one hour at room temperature. The precipitated silver chloride was removed using a syringe filter (PTFE, 0.45 mm) and the solution was added to a suspension of ligand **L1** (0.300 g, 1.25 mmol) in acetonitrile (10 mL). The reaction mixture was then stirred for one hour at room temperature. The desired complex (**1**) was isolated by filtration, washed with acetonitrile and dried under vacuum. Yield: 0.134 g, (59 %) ^{1}H NMR (300 MHz, [D_6]DMSO) δ = 10.20 (br s, 2H Ar-OH), 8.62 (s, 2H, N=C-H), 7.90 (d, 4H, ^3J = 6.3 Hz Ar-H), 6.99 (d, 4H, ^3J = 8.8 Hz Ar-H), 3.90 (s, 4H, CH_{COD}), 2.35 (m, 4H, *J* = 9.8 Hz CH_{2COD}), 1.86 (d, 4H, *J* = 8.0 Hz CH_{2COD}). ^{13}C NMR (151 MHz, [D_6]DMSO) δ = 158.34, 157.00 (C_{imine}), 141.65, 123.89, 116.36 (s),86.82 (C_{COD}) 30.68 (C_{COD}). FT-IR (ATR, cm^{-1}) ν = 3424 (C- O), 2841 (C–H_{COD}), 1607(C=N), 1581 (C=C).

Rhodium(I) Complex 2: A mixture of silver tetrafluoroborate (0.160 g, 0.823 mmol) and [Rh(COD)Cl]$_2$ (0.203 g, 0.411 mmol) was stirred in acetonitrile (10 mL) for one hour at room temperature. The precipitated silver chloride was removed using a syringe filter (PTFE, 0.45 mm) and the solution was added to a suspension of ligand **L2** (0.300 g, 0.823 mmol) in acetonitrile (10 mL). The reaction mixture was then stirred for one hour at room temperature. The desired complex (**2**) was isolated by filtration, washed with acetonitrile and dried under vacuum. Yield: 0.214 g, (61 %) ^{1}H NMR (300 MHz, [D_6]DMSO) δ = 9.99 (br s, 2H Ar-OH), 8.28 (d, 2H, *J* = 8.2 Hz, ArH), 7.65 (t, ^2J = 6.9 Hz, 2H, ArH), 7.24 (d, 4H, ^3J = 6.7 Hz), 7.01 (d, 4H, ^3J = 7.0 Hz), 6.64 (d, 2H, *J* = 1.5 Hz), 3.98 (s, 4H, CH_{COD}), 2.43 (d, 4H *J* = 1.5 Hz CH_{2COD}), 1.87 (d, 4H *J* = 4.1 Hz CH_{2COD}). FT-IR (ATR, cm^{-1}) ν = 3325 (C- O), 2880 (C–H_{COD}), 1623(C=N), 1593 (C=C).

Rhodium(I) Complex 3: A mixture of silver tetrafluoroborate (0.0250 g, 0.128 mmol) and [RhCl(COD)]$_2$ (0.0300 g, 0.0607 mmol) was stirred in acetonitrile (10 mL) for one hour at room temperature. The precipitated silver chloride was removed using a syringe filter (PTFE, 0.25 µm) and the resulting solution was reduced under vacuum and ligand **L3** (0.0600 g, 0.113 mmol), dissolved in DMSO, was added and stirred for 0.5 h at room temperature. The reaction mixture was poured in to acetone. The precipitate that formed was washed with acetone and dried under vacuum for 8 h. Yield: 0.0530 g, (56 %). ^{1}H NMR (300 MHz, [D_6]DMSO): δ (ppm) = 8.68 (s, 2H, H_{imine}), 7.97 (d, *J* = 8.4 Hz, 4H, Ar), 7.17 (d, *J* = 9.0 Hz, 4H, Ar), 4.20 (t, *J* = 6.5 Hz, 4H), 3.92 (s, 4H, CH_{COD}), 2.63–2.56 (m, 4H), 2.36 (s, 4H, CH_{2COD}), 2.09–2.01 (m, 4H), 1.77 (d, *J* = 5.9 Hz, 4H, CH_{2COD}). FT-IR (ATR, cm^{-1}) ν = 1185 and 1054 (O=S=O). 1599 (C=N), 1571 (C=C). **Rhodium(I) Complex 4:** A mixture of silver tetrafluoroborate (0.0240 g, 0.123 mmol, 1.0 equiv.) and [RhCl(COD)]$_2$ (0.0300 g, 0.0607 mmol, 0.5 equiv.) was stirred in acetonitrile (10 mL) for one hour at room temperature. The precipitated silver chloride was removed using a syringe filter (PTFE, 0.25 µm) and the resulting solution was reduced under vacuum and ligand **L4** (0.0793 g, 0.122 mmol) dissolved in DMSO was added and stirred for 0.5 h at room temperature. The reaction mixture was poured in to acetone. The resultng precipitate was washed with acetone and dried under vacuum for 8 h. Yield: 0.0520 g, (62 %). ^{1}H NMR (300 MHz, [D_6]DMSO): δ (ppm) = 8.26 (d, *J* = 8.3 Hz, 2H, H_{imine}), 7.67 (t, *J* = 7.8 Hz, 2H, Ar), 7.35 (d, *J* = 8.6 Hz, 4H, Ar), 7.18 (d, *J* = 8.7 Hz, 4H, Ar), 6.60 (d, *J* = 7.2 Hz, 4H, Ar), 4.19 (t, *J* = 6.3 Hz, 4H), 3.97 (s, 4H, CH_{COD}), 2.62 (d, *J* = 7.1 Hz, 4H), 2.43 (d, *J* = 8.4 Hz, 4H, CH_{2COD}), 2.10–2.03 (m, 4H,), 1.86 (d, *J* = 8.6 Hz, 4H, CH_{2COD}). FT-IR (ATR, cm^{-1}) ν = 1181 and 1036 (O=S=O). 1601 (C=N), 1571 (C=C).

Catalytic Experiment: Hydroformylation reactions were conducted using a 90 mL stainless-steel pipe reactor equipped with a Teflon-coated magnetic stirrer bar. The reactor was charged with the Rh^I catalyst precursor (2.87×10^{-3} mmol), substrate [1-octene (6.37 mmol)], internal standard *n*-decane (1.435 mmol) and either toluene (5 mL) for catalyst precursors **1** and **2** or water (5 mL) for catalyst precursors **3** and **4**. The reactor was and purged with nitrogen three times, followed by purging with syngas (CO/H_2, 1:1) twice. The reactor was pressurised with syngas to the desired pressure and heated to the required temperature. Samples collected at the beginning and at the end of the reaction were analysed by gas chromatography, and the products were confirmed against isooctene and aldehyde standards. All catalytic reactions were performed in triplicate in order to ensure reproducibility and are recorded as an average of three identical experiments.

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Keywords: Hydroformylation · Rhodium · Diimine ligands · Homogeneous catalysis

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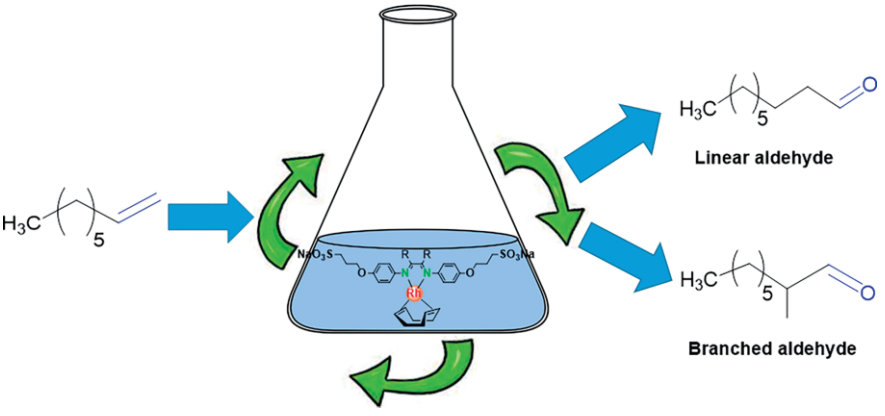

Two water-soluble rhodium(I) complexes based on sulfonated alpha-diimine scaffolds have been synthesised and characterised by NMR and IR spectroscopy, and mass spectrometry. They are catalyst precursors for the aqueous hydroformylation of 1-octene, leading to high, chemoselective conversions of the substrate to aldehydes and the regioselective formation of largely linear products.

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