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PAPER

Aqueous-phase hydroformylation of 1-octene using hydrophilic sulfonate salicylaldimine dendrimers†‡

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Water-soluble dendritic ligands based on tris-2-(5-sulfonato salicylaldimine ethyl)amine (**5**) and DAB-(5-sulfonato salicylaldimine) (**6**) (DAB = diaminobutane) were synthesized by means of Schiff base condensation and sulfonation reactions. These dendritic ligands were fully characterized by ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopy, elemental analysis and mass spectrometry. Dendritic ligands (**5** and **6**) in combination with $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) were evaluated in aqueous biphasic hydroformylation of 1-octene. New water-soluble mononuclear 5-sulfonato propylsalicylaldimine Rh(I) complexes (**7** and **8**) were synthesized and characterized using ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopy, elemental analysis as well as mass spectrometry. These complexes were applied as catalyst precursors in aqueous biphasic hydroformylation reactions. All the catalyst precursors were active in the hydroformylation of 1-octene under the investigated conditions. Optimal conditions were realized at 75 °C (40 bars), where the best selectivity for aldehydes was noticed. Catalyst recycling was achieved up to 5 times with minimal loss in conversion and consistent chemoselectivities and regioselectivities. Less Rh leaching was observed in the dendritic systems (**5** and **6**)/$[RhCl(COD)]_2$ as compared to mononuclear catalyst precursors (**7** and **8**) as determined by inductively coupled plasma-mass spectrometry (ICP-MS).

Introduction

Aqueous biphasic catalysis (Fig. 1) combines the advantages of homogeneous and heterogeneous catalysis. This type of system involves the presence of two phases in one reactor: the aqueous phase in which the catalyst is dissolved, and the organic phase containing the substrate. During the catalytic process, heat, pressure and vigorous stirring allow the two phases to come into contact and the catalytic reaction to occur. At the end of the reaction the organic phase, now containing the products, can be decanted from the immobilized aqueous catalyst, which can then be recycled into further catalytic reactions.[1–3] The process, then, allows the facile separation of a homogeneous catalyst from the reaction products.[1–3]

This type of catalytic process is attractive because it reduces the need for hazardous organic solvents and makes use of water which is non-toxic and environmentally friendly. Recently there has been great interest in the development of water-soluble metal complexes as catalyst precursors for a wide range of reactions, including hydrogenation, hydroformylation, carbonylation and alkene metathesis.[4–16]

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†Dedicated to Professor David Cole-Hamilton on the occasion of his retirement and for his outstanding contribution to transition metal catalysis.

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Biphasic catalysis has found success industrially: the Rûhrchemie/Rhône Poulenc process utilizes a water-soluble rhodium catalyst containing sulfonated phosphine ligands (Fig. 2) in the hydroformylation of propene to butyraldehyde.[1a,2a] This process has been found to be extremely efficient, with the catalyst showing high activity and selectivity for the desired product, the linear aldehyde. It is economically advantageous, there is low catalyst leaching and high catalyst recycling. Furthermore, the use of water as solvent and the avoidance of separation processes such as distillations address some safety, environmental stewardship and economical considerations.[1,2]

Unfortunately, there is one major drawback to the process described above. The substrate must be sufficiently soluble in the aqueous phase in order for chemical transformation to occur. The Rûhrchemie/Rhône Poulenc reaction is limited to the shorter chain olefins propene and 1-butene due to the poor solubility of higher olefins, such as 1-octene, in water.[1,2,17] An interesting strategy for overcoming this particular challenge lies in the use of so-called thermoregulated biphasic systems, whereby the catalyst switches from one phase to the other depending on the temperature.[18,19] Alternatively, the use of amphiphilic ligands could increase the affinity of the catalyst for the organic phase during the catalytic reaction, while allowing the catalyst to retain its water-soluble nature. The use of sulfonated phosphines incorporating long aliphatic pendant arms, for example, has yielded good results in the hydroformylation of 1-tetradecene.[20]

In this paper, *in situ* generation of water soluble Rh(I) metallodendrimers based on tris-2-(iminoethyl)amine and poly(propyleneimine) dendritic scaffolds (bearing sulfonate groups) for the

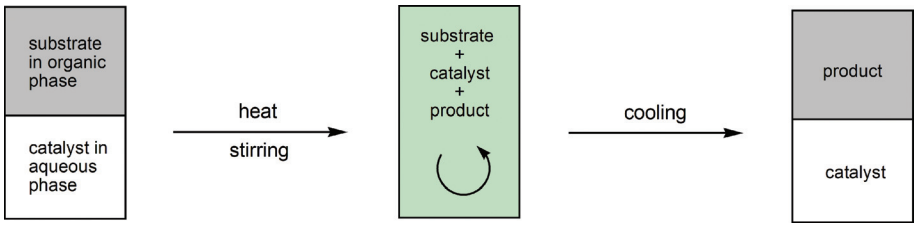


Fig. 1 Diagram showing principle of aqueous biphasic catalysis.

aqueous biphasic hydroformylation of 1-octene is described. In addition, new water-soluble mononuclear complexes prepared by the reaction of $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) with sulfonated propylsalicylaldimine ligands are reported and their catalytic behaviour in the hydroformylation reaction is also investigated and discussed.

Results and discussion

Synthesis and characterization of 5-sulfonatosalicylaldehydes (1 and 2)

Both monomeric and dendritic ligands based on propylamine, tris-2-(aminoethyl)amine and diaminobutane (DAB) have been investigated. The dendrimer ligands were of interest as metallodendrimers often display an enhanced catalytic activity and stability (known as positive dendritic effect) relative to their mononuclear counterparts.[21] In addition, there have been few reports on the use of water-soluble metallodendrimers as catalyst precursors in aqueous biphasic catalytic reactions.[22,23]

The anionic sulfonated salicylaldehyde starting materials (**1** and **2**) were prepared according to modified literature procedures as shown in Scheme 1.[24,25] Both sulfonated salicylaldehydes (**1** and **2**) were afforded as crystalline solids in good yields (63 and 87% respectively) and have been characterized using ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopy, elemental analysis (C, H, N and S) and mass spectrometry.

^{1}H NMR spectra for compounds (**1** and **2**) displays signals for the hydroxyl hydrogen at *ca.* δ 9.96 ppm as well as aromatic peaks in the region of δ 8.11–7.70 ppm. In the ^{13}C NMR spectra, the carbonyl carbons exhibit characteristic signals at *ca.* δ 192 ppm, while the aromatic carbons are seen between *ca.* δ 165–123 ppm. FT-IR spectroscopic results show absorption bands at 1665 cm^{-1} for (**2**) and 1667 cm^{-1} for (**1**) due to the carbonyl functionality as well as strong ν(O–H) bands.

Synthesis and characterization of 5-sulfonato propylsalicylaldimine ligands (3 and 4)

Subsequently, N^O bidentate monomeric 5-sulfonato salicylaldimine ligands (**3** and **4**) were prepared by the Schiff base condensation reactions of *n*-propylamine with 5-sulfonato salicylaldehydes (**1** or **2**) and were isolated as yellow, air-stable solids (eqn (1)). Compound (**3**) is soluble in water and dimethylsulfoxide (DMSO) while (**4**), containing a hydrophobic substituent, is soluble in alcohols such as methanol and ethanol as well. Infrared spectroscopy confirmed the disappearance of the starting aldehyde (ν(C=O) = 1665 cm^{-1} and 1667 cm^{-1}) and the

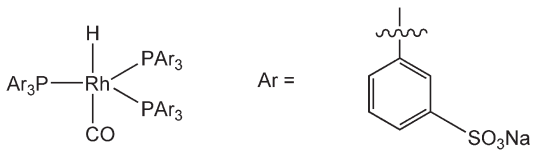
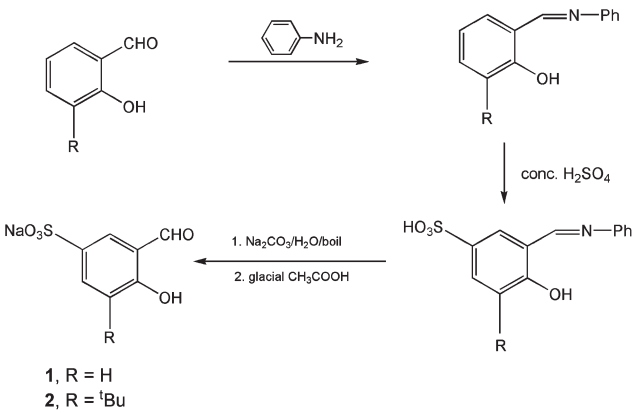
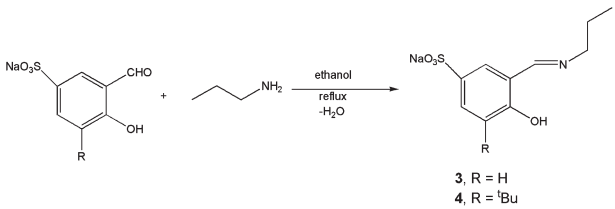


Fig. 2 Water-soluble rhodium catalyst used in the industrial hydroformylation of lower olefins.



Scheme 1 Outline of the preparation of monosodium 5-sulphonatosalicylaldehydes (**1** and **2**).

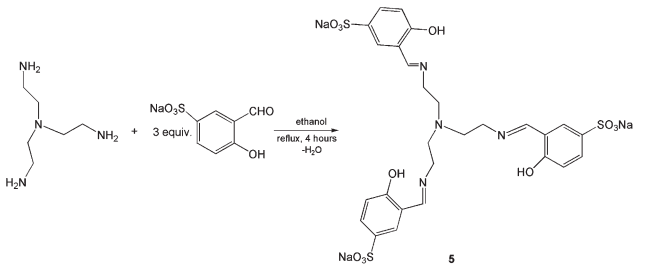
formation of imines by the strong ν(C=N) bands at 1636 cm^{-1} (**4**) and 1638 cm^{-1} (**3**). The ^{1}H NMR spectra of ligands (**3** and **4**) exhibit imine signals at *ca.* δ = 8.60 ppm for both complexes. ^{13}C NMR revealed the expected number of peaks in the aromatic and aliphatic regions, as well as imine peaks in the expected region, above δ = 170 ppm. C, H, N and S analysis is in agreement with the proposed structures and the respective mass spectra (ESI-MS) showing the $[M - Na + 2H]^+$ (*m*/*z* = 244.10, **3**) and $[M - Na]^+$ (*m*/*z* = 298.10, **4**) ions, are also in support of the formation of these ligands.



(1)

Synthesis and characterization of tris-2-(5-sulfinatosalicylaldimine ethyl)amine ligand (5)

The tris-2-(aminoethyl)amine analogue of (**3**) was prepared in a similar manner; however a longer reflux time and a slight excess of the starting aldehyde ensured complete functionalization of the pendant amino groups (eqn (2)). This low generation dendritic ligand (**5**) was isolated as a powdery yellow hygroscopic solid in good yield (96%).



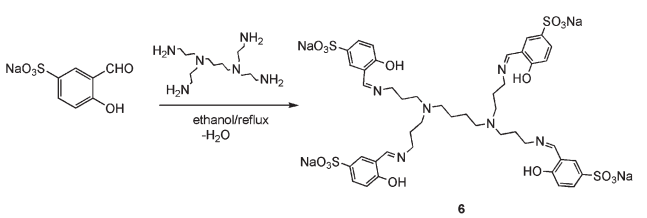
(2)

The compound is soluble in water and DMSO and has been characterized using elemental analysis (C, H, N and S), FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy as well as mass spectrometry.

Several attempts to obtain good elemental analysis of ligand (**5**) were unsuccessful due its highly hygroscopic nature. The infrared spectrum of ligand (**5**) shows a strong characteristic imine band at 1636 cm^{-1} as well as a ν(O–H) absorption band. Both the ^{1}H and ^{13}C NMR spectra indicate the formation of the imine moiety through signals at δ = 8.56 ppm (^{1}H) and *ca.* δ = 167 ppm (^{13}C) and all other expected signals are observed. Electron impact mass spectrometry (EI-MS) agrees with the formation of this ligand by displaying a peak at m/z = 704.72 for the $[M - 3Na - 2H]^{+}$ ion.

Synthesis and characterization of DAB-(5-sulfinatosalicylaldimine) ligand (6)

A first-generation poly(propyleneimine) ligand was prepared by the reaction of sodium 5-sulfonato salicylaldehyde with the first-generation DAB dendrimer in ethanol (DAB = diaminobutane) (eqn (3)). Although there are several examples of water-soluble Schiff base ligands prepared by the condensation of sodium 5-sulfonato salicylaldehyde with various amines,[24–27] to our knowledge there are no reports of the preparation of water-soluble DAB dendrimers by this method.



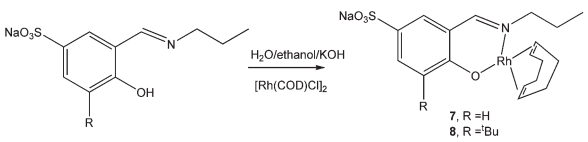
(3)

Dendrimer (**6**) was isolated as a yellow solid (yield: 66%) which like compound (**5**) is water soluble and highly hygroscopic. This dendritic ligand has been characterized fully using ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopy, elemental analysis (C, H, N and S) and mass spectrometry.

The infrared spectrum displays the characteristic C═N imine stretching frequency at 1635 cm^{-1}. The ^{1}H NMR spectrum displays peaks following a similar trend to the corresponding monomeric analogue (**3**), except for peak broadening in the aliphatic region, due to the macromolecular nature of the dendritic ligand (**6**). Therefore, there is a signal at δ = 8.55 ppm assigned to the imine protons, broad aliphatic signals in the region of δ = 1.30–3.60 ppm and aromatic signals ranging from δ = 6.78–7.69 ppm in the ^{1}H NMR spectrum of ligand (**6**). Similarly in the ^{13}C NMR spectrum, a distinct imine carbon signal is evident at *ca* δ = 166 ppm along with aromatic and aliphatic carbon signals between *ca.* 24–162 ppm. ESI-MS results show the presence of the $[M - 4Na - 4H]+$ (m/z = 1060.58) ion, while fitting elemental analysis results could not be obtained here too due to the hygroscopic nature of the dendritic ligand and possible solvent inclusion within the dendritic arms.[28*a–d*]

Synthesis and characterization of substituted and unsubstituted 5-sulfonato propylsalicylaldimine Rh(I) complexes (7 and 8)

The monomeric ligands (**3** and **4**) were reacted with the Rh(I) precursor $[Rh(COD)Cl]_2$ according to eqn (4).



(4)

The metal complexes were isolated as yellow solids and are somewhat less soluble in water than the free ligands, probably due to the presence of the hydrophobic rhodium COD moiety. However, they do retain some aqueous solubility, and are also quite soluble in DMSO and methanol. These new complexes have been fully characterised using elemental analysis (C, H, N and S), FT-IR and ^{1}H NMR and ^{13}C NMR spectroscopy as well as mass spectrometry.

Elemental analysis results gave C, H, N and S percentage values corresponding to the calculated percentages. Infrared spectroscopy of complexes (**7** and **8**) indicates coordination of the metal centre to the imine nitrogen, where ν(C═N) has shifted to 1606 cm^{-1} and 1607 cm^{-1}, from 1638 cm^{-1} in ligand (**3**) and 1636 cm^{-1} in ligand (**4**), respectively. The ^{1}H NMR spectra of the monomeric complexes exhibit some interesting features. Firstly, there is an upfield shift of the imine proton to approximately δ = 8.10 ppm in the proton spectrum (Fig. 3). Secondly, there is splitting of the vinylic COD protons, due probably to the asymmetric environment induced by the chelating N–O ligand. The ^{13}C spectrum supports this, where two separate signals are observed for the vinylic carbons. In some instances these signals are observed as doublets, due to coupling to the NMR-active ^{103}Rh ($^{1}J_{Rh-C}$ = 13 Hz), but in this particular spectrum the vinylic carbon peaks are rather broad, and the splitting is not always clear. Carbon NMR also shows an upfield shift of the C═N peak. All remaining expected peaks were observed in the correct regions for both the ^{1}H and ^{13}C NMR spectra.

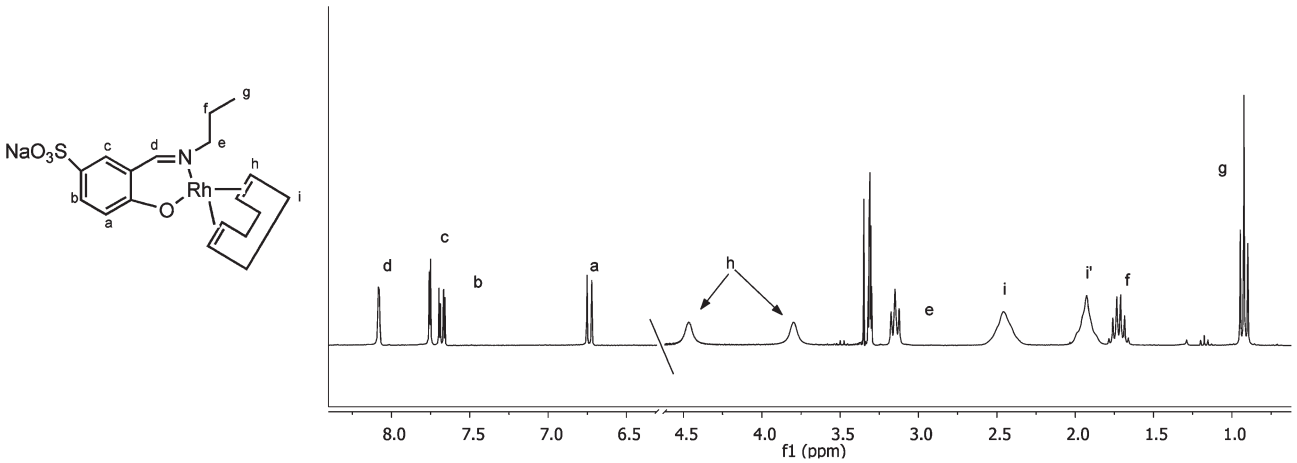


Fig. 3 ^{1}H NMR spectrum of rhodium complex (**7**) conducted at 25 °C in D_2O.

Table 1 Aqueous biphasic hydroformylation of 1-octene at different temperatures over 8 hours[a]

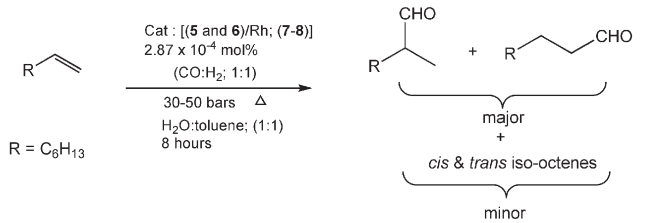
Entry	Cat.	Temp. (°C)	Conversion (%)	Aldehydes (%)	Iso-octenes (%)	*n* : iso[b]	TOF[c] (h^{-1})
1	**5**/[RhCl(COD)]$_2$	75	79	52	48	72 : 28	189
2	**6**//[RhCl(COD)]$_2$	75	99	37	63	57 : 48	134
3	**7**	75	72	85	15	56 : 44	309
4	**8**	75	75	56	44	74 : 26	203
5	**5**/[RhCl(COD)]$_2$	95	89	64	36	46 : 54	233
6	**6**//[RhCl(COD)]$_2$	95	92	71	29	39 : 61	258
7	**7**	95	77	88	12	46 : 54	320
8	**8**	95	87	63	37	31 : 69	229

[a] Reactions carried out with (CO : H_2) (1 : 1) at 30 bars in distilled H_2O (5 ml) and toluene (5 ml) with 6.37 mmol of 1-octene and 2.87 × 10^{-3} mmol Rh catalyst precursor (error estimate: (**5**/RhCl(COD)]$_2$) = ±0.16; (**6**/RhCl(COD)]$_2$) = ±0.14; (**7**) = ±0.16 and (**8**) = ±0.12). GC conversions obtained using *n*-decane as an internal standard in relation to authentic standard iso-octenes and aldehydes. [b] Regioselectivity calculated at 2 hours. [c] TOF = (mol product/mol cat.) × h^{-1} and is based on total aldehydes produced.

The mass spectral data for complexes (**7** and **8**) agrees with the proposed structures, where peaks corresponding to $[M +/- Na]^+$ are observed.

Aqueous biphasic hydroformylation of 1-octene

The catalytic behaviour of Rh(I) metallodendrimers generated *in situ* from [RhCl(COD)]$_2$ and the water-soluble dendritic ligands (**5** and **6**) were evaluated in the aqueous biphasic hydroformylation of 1-octene. In each experiment, the substrate (1-octene) was in toluene while the catalyst precursor was immobilized in a water layer (eqn (5)).



(5)

Effect of temperature. Previous studies using iminophosphine and iminopyridyl based Rh(I) catalyst precursors in the hydroformylation of 1-octene revealed 75 °C and 95 °C (30 bars) as suitable temperatures and pressure to obtain high yields of aldehydes.[28d,29] Therefore, initial reactions in this study were carried out under these conditions and the results are summarized in Table 1.

All the catalyst precursors are active at 75 °C (30 bars) with conversion in the ranges of 72–99%. The dendritic systems (**5** and **6**)/[RhCl(COD)]$_2$ display better conversion compared to the mononuclear systems (**7** and **8**) (Table 1, entries 1–4). Aldehyde formation is most favoured when using catalyst precursor (**7**) while, (**8**) and (**5**)/[RhCl(COD)]$_2$ yield near equal amounts of aldehydes and iso-octenes. The linear aldehyde (nonanal) is favoured in all the reactions. Turnover frequency (TOF) calculations based on total aldehydes formed indicate that the mononuclear systems perform better than their dendritic counterparts, possibly due to lesser steric bulk in (**7** and **8**) as compared to the macromolecular dendritic systems (**5** and **6**)/[RhCl(COD)]$_2$. Steric hindrances can impede activity and the rate of hydroformylation. Increasing the temperature to 95 °C (30 bars) results in increased conversion of 1-octene and more aldehydes forming (Table 1, entries 5–8). Branched aldehydes are dominant at this

Table 2 Aqueous biphasic hydroformylation of 1-octene at different pressures over 8 hours[a]

Entry	Cat.	Pressure (bars)	Conversion (%)	Aldehydes (%)	Iso-octenes (%)	*n* : iso[b]	TOF[c] (h^{-1})
1	**5**/$[RhCl(COD)]_2$	40	94	81	19	60 : 40	294
2	**6**/$[RhCl(COD)]_2$	40	90	86	14	61 : 39	312
3	**7**	40	98	96	4	56 : 44	349
4	**8**	40	96	92	8	62 : 38	334
5	$[RhCl(COD)]_2$	40	99	99	1	49 : 51	359
6	**5**/$[RhCl(COD)]_2$	50	82	46	54	66 : 34	167
7	**6**//$[RhCl(COD)]_2$	50	74	46	54	59 : 41	167
8	**7**	50	88	62	38	54 : 46	225
9	**8**	50	90	51	49	61 : 39	185

[a] Reactions carried out with ($CO : H_2$) (1 : 1) at 75 °C in distilled H_2O (5 ml) and toluene (5 ml) with 6.37 mmol of 1-octene and 2.87×10^{-3} mmol Rh catalyst precursor (error estimate: (**5**/$RhCl(COD)]_2$) = ±0.13; (**6**/$RhCl(COD)]_2$) = ±0.11; (**7**) = ±0.10 and (**8**) = ±0.09). GC conversions obtained using *n*-decane as an internal standard in relation to authentic standard iso-octenes, aldehydes, alcohols and *n*-octane. [b] Regioselectivity calculated at 2 hours. [c] TOF = (mol product/mol cat.) × h^{-1} and is based on total aldehydes produced. Trace amounts of alcohols and *n*-octane were detected by GC for reactions at 50 bars.

temperature and these are afforded *via* initial isomerization reactions as observed by monitoring the reactions using gas chromatography (GC) every 2 hours.[29] However, the catalyst precursors all display decomposition to a black species in solution at 95 °C (30 bars).

Effect of pressure. Further experiments were carried out to explore how increasing the syngas pressure affects hydroformylation activity and selectivity (Table 2).

Increasing the pressure from 30 bars (Table 1, entries 1–4) to 40 bars (75 °C) results in a marked improvement in conversion of 1-octene and TOFs thus leading to high yields in aldehydes (Table 2, entries 1–4). The linear aldehyde (nonanal) is favoured while there is a slight decrease in the average *n* : iso ratio in comparison to reactions carried out at 30 bars (75 °C). The mononuclear systems (**7** and **8**) tend to perform better than the dendritic systems (**5** and **6**)/$[RhCl(COD)]_2$ in producing the most aldehydes and therefore higher TOFs here. This is indicative of better accessibility of the substrate to active Rh sites in the mononuclear systems and therefore increased hydroformylation rates. A reaction carried out using the dimeric precursor $[RhCl(COD)]_2$ (entry 5) also displays excellent conversion of 1-octene to aldehydes. However there is no outright regioselectivity in this case. Moreover, this catalyst precursor is soluble in the organic layer and therefore cannot be recycled and reused by means of aqueous/organic phase separations, as is the intention of this study. Further increasing the pressure to 50 bars (75 °C) produces a slight drop in 1-octene conversion and a more pronounced decrease in aldehyde formation (Table 2 entries 6–9). Encouragingly, the linear aldehyde is favoured in these reactions too. In addition, trace amounts of alcohols and *n*-octane were observed by GC analysis when operating at 50 bars (75 °C) and 40 bars (95 °C).[30]

Chemoselectivity and regioselectivity. These studies have revealed that the current catalyst precursors produce the best chemoselectivity for aldehydes at 40 bars (75 °C), where the aldehydes yielded range from 81–96% (Table 2). On the other hand, slightly more iso-octenes are formed at 50 bars (75 °C) as well as trace amounts of hydrogenation products. Overall, nonanal is preferred at 75 °C (30 and 40 bars) (Tables 1 and 2), an

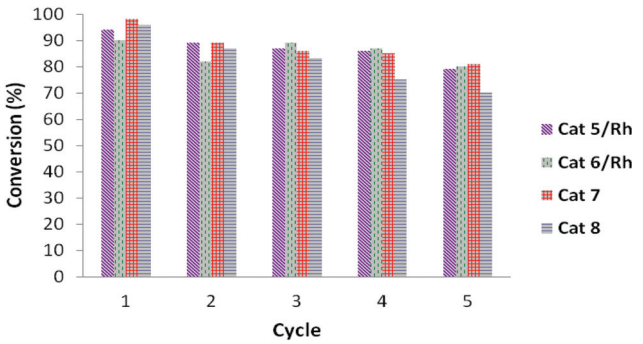


Fig. 4 Recycle runs of catalyst precursors (**5** and **6**)/$[RhCl(COD)]_2$ and (**7** and **8**). Reactions carried out with ($CO : H_2$) (1 : 1) at 75 °C (40 bars) in distilled H_2O (5 ml) and toluene (5 ml) with 6.37 mmol of 1-octene and 2.87×10^{-3} mmol Rh catalyst precursor (error estimate: (**5**/$RhCl(COD)]_2$) = ±0.14; (**6**/$RhCl(COD)]_2$) = ±0.12; (**7**) = ±0.10 and (**8**) = ±0.11).

observation that has been reported.[29,31,32] The N^O based chelating systems in the current study show inferior regioselectivity as compared to N^N and N^P based chelating systems that we have recently reported for hydroformylation of 1-octene.[29] There are no significant differences between reactions carried out using dendritic catalyst precursors (**5** and **6**)/$[RhCl(COD)]_2$ and mononuclear analogues (**7** and **8**) with regards to chemo- and regioselectivities, however the dendritic scaffolds appear to stabilize and restrict Rh leaching to a greater extent than their mononuclear counterparts (*vide infra*). This Rh retention may be promoted by a combination of the N^O chelate moiety and the N atoms within the dendritic scaffolds.

Recyclability and Rh leaching studies. The catalyst precursors exhibit good recyclability over at least five cycles (Fig. 4) and chemoselectivities as well as regioselectivities remained consistent throughout the cycles. After simple decantation of the organic layer, the aqueous layer containing the active catalyst was reused in subsequent reactions. There is an average loss in conversion of *ca.* 6% for (**5** and **6**)/$[RhCl(COD)]_2$ and *ca.* 14% for (**7** and **8**) after the first run and this may be attributed to Rh leaching from the aqueous layer and catalyst decomposition.

ICP-MS analysis of the aqueous layer shows that 11% and 9% Rh has leached from the aqueous layer during reactions involving (**5**)/$[RhCl(COD)]_2$ and (**6**)/$[RhCl(COD)]_2$ respectively. Even greater quantities of Rh, 19% and 22% for (**7**) and (**8**) respectively, are leached from the reactions involving the mononuclear catalyst precursors due to reasons proposed earlier in the text. Additionally, the use of hard and strong donors such as the imine and phenoxide may destabilize the catalyst precursor thus resulting in more leaching in comparison to *pi*-acidic ligands (*e.g.* traditionally used phosphine-based ligands).

Conclusions

Water-soluble dendritic ligands derived from tris-2-(aminoethyl)-amine and diaminobutane (DAB) cores were synthesized and these were characterized by a combination of analytical and spectroscopic techniques. These ligands were successfully employed as precursors to water-soluble Rh(I) metallodendrimers for aqueous biphasic hydroformylation of 1-octene. Additionally, new model water-soluble mononuclear complexes were obtained and fully characterized for application in the hydroformylation reaction. All the catalyst precursors proved active and selective in the hydroformylation of 1-octene to aldehydes (major products). These systems possess the ability to interact with a long chain α-olefin during catalysis under aqueous biphasic conditions and we believe that the aliphatic groups in compounds (**5**–**8**) play a role in ensuring this interaction. Optimal conditions were established at 40 bars (75 °C) where the most aldehydes were afforded. Branched aldehydes were predominantly obtained at 30 and 40 bars (95 °C) and nonanal at 30 and 40 bars (75 °C). This phenomenon introduces the idea of thermal and pressure regulated regioselectivity. Incorporation of sulfonate groups presents promising catalyst precursors which can be immobilized in water, a green solvent, and subsequently recycled up to five times with consistent activities and selectivities.

Experimental

General details

All reactions were carried out in air unless otherwise stated. Solvents used were reagent grade and were not distilled prior to use unless otherwise stated. $RhCl_3{\cdot}3H_2O$ was obtained from Anglo Platinum Corporation. All other chemicals were purchased from Aldrich and used as received. $[Rh(COD)Cl]_2$ was prepared according to a literature procedure.[13]

^1H and ^{13}C NMR spectra were recorded on a Varian Mercury-300 MHz (^1H: 300 MHz; ^{13}C: 75.5 MHz; ^{31}P: 121 MHz) or Varian Unity-400 MHz (^1H: 400 MHz; ^{13}C: 100.6 MHz) spectrometer and values are reported relative to the internal standard tetramethylsilane (δ 0.00). FT-IR spectra were recorded as KBr pellets using a Perkin Elmer 100 Spectrum One spectrometer. Elemental analyses were conducted with a Fision EA 110 CHNS Analyzer. Melting points were determined using a Kofler hot stage microscope (Riechter Thermo). Electrospray Ionization (ESI) mass spectrometry was carried out on a Waters API Quattro Micro triple quadrupole mass spectrometer in the positive or negative-ion mode. Electron Impact mass spectrometry was conducted on an Agilent 6890 N spectrometer. Inductively coupled plasma-mass spectrometry was obtained using a Perkin-Elmer Elan600 quadrupole ICP-MS with a Cetax LSX-200 UV laser module. Catalysis products were analysed using a Perkin Elmer Clarus 580 GC.

Synthesis of monosodium 5-sulfonatosalicylaldehydes (1 and 2)

The sulfonated salicylaldehydes (**1** and **2**) were prepared according to modified literature procedures in a stepwise manner as outlined below.

Step 1: synthesis of *N*-phenyl-salicylaldimine. Salicylaldehyde (5.02 g, 41.10 mmol) and aniline (5.84 g, 41.20 mmol) were stirred in 50 cm^3 methanol for 90 minutes. Distilled water was then added dropwise, with stirring, to the yellow solution until the solution remained cloudy for a few seconds before turning translucent again. The mixture was cooled in an ice-bath and the resultant yellow crystalline product was filtered and washed with small portions of cold water and methanol. Yield 7.51 g (93%).

Step 2: synthesis of *N*-phenyl-5-sulfonato-salicylaldimine. Concentrated sulfuric acid (10 cm^3 of 98% H_2SO_4) was placed in a round-bottomed flask fitted with reflux condenser and 3.50 g (17.70 mmol) *N*-phenyl-salicylaldimine was added slowly with stirring. The mixture was heated at 100–105 °C for 2.5 hours. The hot solution was poured carefully into a beaker containing *ca.* 100 cm^3 ice water. A yellow product precipitated immediately. The suspension was then reheated until all the product had dissolved to form a bright orange solution. Undissolved particles were filtered by gravity from the hot solution and the filtrate left to stand at room temperature. The yellow-brown microcrystalline product was filtered and washed with small portions of cold water. Yield 2.79 g (57%).

Step 3: synthesis of monosodium 5-sulfonatosalicylaldehyde (1). *N*-Phenyl-5-sulfonato-salicylaldimine (1.49 g, 5.39 mmol) and Na_2CO_3 (0.60 g, 5.70 mmol) were boiled vigorously in an open flask containing 10 cm^3 distilled water for two hours. The water was replenished as necessary. Glacial acetic acid (6 cm^3) was then added to the cooled solution. The same amount of ethanol was added and the solution cooled in an ice-bath for several hours. The fine beige crystals of (**1**) were filtered and washed with cold ethanol, and dried *in vacuo*. Yield: (0.76 g, 63%). mp.: 331–334 °C. FT-IR (ν_{max}/cm^{-1}, KBr): 3460s (O–H), 1667s (C═O). δ_H (400 MHz, D_2O, 25 °C) (ppm) = 9.95 (s, 1H, C(O)**H**), 8.11 (d, ^4J = 2.39 Hz, 1H, **Ar**), 8.07 (d, ^3J = 8.78 Hz, 1H, **Ar**), 7.92 (dd, ^3J = 8.78 Hz, ^4J = 2.39 Hz, 1H, **Ar**). δ_C (75 MHz, DMSO-d_6, 25 °C) (ppm) = 191.9, 165.3, 162.0, 136.8, 131.8, 125.5, 123.3. Elemental Analysis (calculated for $C_7H_5NaO_5S$): C, 37.51; H, 2.28; S, 14.30. Found: C, 37.28; H, 2.16; S, 14.04%. EI-MS (*m*/*z*) = 200.07 ($[M - Na - H]^+$, 59%).

Step 1: synthesis of *N*-phenyl-3-^{t}butyl-salicylaldimine. 3-*tert*-Butyl-2-hydroxybenzaldehyde (0.94 g, 5.27 mmol) and aniline (0.49 g, 5.30 mmol) were stirred in 20 cm^3 of ethanol. Anhydrous magnesium sulfate was added and the reaction mixture stirred overnight. The solvent was removed to yield a yellow oil; this was used directly as obtained in the following reaction.

Step 2: synthesis of *N*-phenyl-3-^{t}butyl-5-sulfonatosalicylaldimine. The round-bottomed flask containing *N*-phenyl-3-^{t}butyl-

salicylaldimine was submerged in an ice-bath; 6 cm^3 concentrated (98%) sulfuric acid was added slowly with stirring. The orange solution was then heated at 105–110 °C for 2.5 hours. The solution was allowed to cool and ice pieces were added to induce crystallization. A peach coloured precipitate formed; this was filtered and washed with ice-cold water and dried *in vacuo*. Yield 0.77 g (44% based on initial aldehyde used).

Step 3: synthesis of monosodium 3-*t*butyl-5-sulfonatosalicylaldehyde (2). The *N*-phenyl-3-*t*butyl-5-sulfonatosalicylaldimine was dissolved in hot distilled water and an equimolar amount of Na_2CO_3 was added slowly over several minutes. The solution was left to boil in an open flask for three hours, with periodic replenishment of water, as needed. Then 3 cm^3 each of acetic acid and ethanol were added. The product did not precipitate after extended cooling, therefore the solution was heated again until all solvent had evaporated. Ethanol was added and the light brown crystalline product (**2**) was filtered and washed well with ethanol to remove all traces of acetic acid. Yield: (0.71 g, 87%). mp 158–161 °C. FT-IR (ν_{max}/cm^{-1}, KBr): 3441s (O–H), 1665s (C═O). δ_H (400 MHz, D_2O, 25 °C) (ppm) = 9.96 (s, 1H, C(O)**H**), 7.79 (d, ^4J = 2.60 Hz, 1H, **Ar**), 7.70 (d, ^4J = 2.62 Hz, 1H, **Ar**), 1.31 (s, 9H, C**H**$_3$). δ_C (75 MHz, DMSO-d_6, 25 °C) (ppm) = 192.1, 164.8, 160.9, 135.7, 132.4, 126.7, 126.4, 34.3, 30.1, 28.5, 25.6. Elemental Analysis (calculated for $C_{11}H_{13}NaO_5S$): C, 47.14; H, 4.68; S, 11.44. Found: C, 46.92; H, 4.12; S, 10.96%. EI-MS (*m*/*z*) = 256.13 ([M − Na − H]$^+$, 63%).

Synthesis of 5-sulfonatosalicylaldimine ligands (3 and 4)

Synthesis of 5-sulfonato propylsalicylaldimine (3). Propylamine (0.028 g, 0.47 mmol) and sodium 5-sulfonatosalicylaldehyde (**1**) (0.106 g, 0.47 mmol) were refluxed in ethanol for 60 minutes. The yellow precipitate of (**3**) was filtered and washed with ethanol. Yield: (0.110 g, 88%). mp.: decomp without melting, onset occurs at 289 °C. FT-IR (ν_{max}/cm^{-1}, KBr): 3521s (O–H), 1638s (C═N). δ_H (400 MHz, DMSO-d_6, 25 °C) (ppm) = 13.8 (s, O**H**), 8.57 (s, 1H, **H**$_{imine}$), 7.68 (d, ^4J = 2.19 Hz, 1H, **Ar**), 7.54 (dd, ^3J = 8.54, ^4J = 2.18 Hz, 1H, **Ar**), 6.77 (d, ^3J = 8.54 Hz, 1H, **Ar**), 3.56 (td, ^3J = 6.76, ^4J = 1.08 Hz, 2H, –NC**H**$_2$), 1.66 (sext., ^3J = 7.10 Hz, 2H, C**H**$_2$), 0.93 (t, ^3J = 7.39, 3H, C**H**$_3$). δ_C (75 MHz, DMSO-d_6, 25 °C) (ppm) = 173.4, 165.9, 161.8, 137.3, 131.6, 126.7, 122.9, 60.2, 22.2, 11.7. Elemental Analysis (calculated for $C_{10}H_{12}NNaO_4S$): C, 45.28; H, 4.56; N, 5.28; S, 12.09. Found: C, 45.48; H, 4.19; N, 5.88; S, 11.86%. ESI-MS (*m*/*z*) = 244.10 ([M − Na + 2H]$^+$, 56%).

Synthesis of 3-*t*butyl-5-sulfonato propylsalicylaldimine (4). Propylamine (0.046 g, 0.78 mmol) was dissolved in 10 cm^3 ethanol; sodium 3-*t*butyl-5-sulfonatosalicylaldehyde (**2**) (0.217 g, 0.78 mmol) was added and the mixture refluxed for 30 minutes. The bright yellow solution was cooled to room temperature and filtered by gravity. The solvent was removed *in vacuo* to reveal an oily yellow product (**4**) which solidified upon standing for several hours. The product was collected and washed with diethyl ether. Yield: (0.202 g, 81%). mp.: 213–215 °C. FT-IR (ν_{max}/cm^{-1}, KBr): 3447s (O–H), 1636s (C═N). δ_H (400 MHz, D_2O, 25 °C) (ppm) = 8.55 (t, ^4J = 1.10 Hz, 1H, **H**$_{imine}$), 7.58 (d, ^4J = 2.18 Hz, 1H, **Ar**), 7.54 (d, ^4J = 2.17 Hz, 1H, **Ar**), 3.56 (td, ^3J = 6.81, ^4J = 1.08 Hz, 2H, –NC**H**$_2$), 1.67 (sext., ^3J = 7.20 Hz, 2H, C**H**$_{2propyl}$), 1.38 (s, 9H, C**H**$_3{}^t{}_{butyl}$), 0.94 (t, ^3J = 7.37 Hz, 3H, C**H**$_{3propyl}$). δ_C (75 MHz, DMSO-d_6, 25 °C) (ppm)= 174.1, 166.8, 162.3, 137.5, 136.4, 127.7, 127.1, 116.9, 59.1, 34.8, 29.4, 23.9, 21.8, 11.8. Elemental Analysis (calculated for $C_{14}H_{20}NNaO_4S$): C, 52.32; H, 6.27; N, 4.36; S, 9.98. Found: C, 52.86; H, 6.79; N, 4.11; S, 10.68%. ESI-MS (*m*/*z*) = 298.10 ([M − Na]$^+$), 66%).

Synthesis of 5-sulfonatosalicylaldimine dendrimers (5 and 6)

Synthesis of tris-2-(5-sulfinatosalicylaldimine ethyl)amine ligand (5). Tris-2-(aminoethyl)amine (0.038 g, 0.26 mmol) and sodium 5-sulfonatosalicylaldehyde (**1**) (0.24 g, 1.07 mmol) were refluxed in ethanol for 4 hours. The yellow hygrosopic solid product (**5**) was filtered under nitrogen and washed with ethanol. Yield: (0.190 g, 96%). mp.: decomp without melting, onset occurs at 291 °C. FT-IR (ν_{max}/cm^{-1}, KBr): 3430s (O–H), 1636s (C═N). δ_H (400 MHz, DMSO-d_6, 25 °C) (ppm) = 8.56 (s, *J* = 6.57 Hz, 3H, **H**$_{imine}$), 7.68 (d, ^4J = 1.81 Hz, 3H, **Ar**), 7.55 (dd, ^3J = 8.57, ^4J = 2.17, **Ar**), 6.78 (dd, ^3J = 8.56, ^4J = 1.86 Hz, 3H, **Ar**), 3.70 (t, ^3J = 6.39 Hz, 6H, –NC**H**$_2$), 2.92 (t, ^3J = 6.69 Hz, 6H, C**H**$_2$). δ_C (75 MHz, DMSO-d_6, 25 °C) (ppm)= 166.9, 162.3, 138.9, 130.4, 129.3, 117.3, 116.5, 56.6, 55.1. Elemental Analysis (calculated for $C_{28}H_{31}N_4Na_3O_{12}S_3$): C, 43.08; H, 4.00; N, 7.18; S, 12.32. Found: C, 40.59; H, 4.34; N, 8.13; S, 11.30%. EI-MS (*m*/*z*) = 704.72 ([M − 3Na − 2H]$^+$), 27%).

Synthesis of DAB-(5-sulfinatosalicylaldimine) ligand 6. DAB generation 1 dendrimer (0.72 g, 0.23 mmol) and sodium 5-sulfonatosalicylaldehyde (**1**) (0.23 g, 1.03 mmol) were refluxed in ethanol for four hours then stirred overnight. The yellow hygrosopic precipitate of (**6**) was filtered under nitrogen and washed with ethanol. Yield: (0.157 g, 66%). mp.: decomp without melting, onset occurs at 271 °C. FT-IR (ν_{max}/cm^{-1}, KBr): 3436s (O–H), 1635s (C═N). δ_H (400 MHz, DMSO-d_6, 25 °C) (ppm) = δ 8.55 (s, 4H, **H**$_{imine}$), 7.69 (d, ^4J = 1.97 Hz, 4H, **Ar**), 7.55 (dd, ^3J = 8.56, ^4J = 1.98 Hz, 4H, **Ar**), 6.78 (d, ^3J = 8.58 Hz, 4H, **Ar**), 3.6–1.3 (m, 32H, C**H**$_2$). δ_C (75 MHz, DMSO-d_6, 25 °C) (ppm) = 166.0, 162.4, 138.7, 130.3, 129.3, 117.3, 116.4, 56.0, 53.7, 51.1, 28.3 (d), 24.7. Elemental Analysis (calculated for $C_{45}H_{56}N_6Na_4O_{16}S_4$): C, 46.71; H, 4.88; N, 7.26; S, 11.08. Found: C, 44.97; H, 5.16; N, 8.64; S, 10.82%. ESI-MS (*m*/*z*) = 1060.58 ([M − 4Na − 4H]$^+$), 38%).

Synthesis of substituted and unsubstituted 5-sulfonato propylsalicylaldimine Rh(I) complexes (7 and 8)

Synthesis of 5-sulfonato propylsalicylaldimine rhodium(I)1,5-cyclooctadiene complex (7). Propylamine (0.019 g, 0.32 mmol) and deprotonated sodium 5-sulfonatosalicylaldehyde (**3**) (0.085 g, 0.34 mmol) were stirred in ethanol–water mixture under argon. After 5 minutes $[Rh(COD)Cl]_2$ (0.072 g, 0.15 mmol) was added and the reaction stirred at room temperature for 1 hour. The solvent was removed; methanol and diethyl ether were added to precipitate the product, which was filtered to give a yellow solid product (**7**). Yield: (0.091 g, 66%). mp.: decomp without melting, onset occurs at 301 °C. FT-IR (ν_{max}/cm^{-1}, KBr): 1606s (C═N). δ_H (400 MHz, D_2O, 25 °C) (ppm) =

8.12 (s, 1H, $\mathbf{H}_{imine}$), 7.75 (d, ^4J = 2.52 Hz, 1H, **Ar**), 7.67 (dd, ^3J = 8.92 Hz, ^3J = 2.53 Hz, 1H, **Ar**), 6.86 (d, ^3J = 8.94 Hz, 1H, **Ar**), 4.40 (br s, 2H, $C\mathbf{H}_{COD}$), 3.88 (br s, 2H, $C\mathbf{H}_{COD}$), 3.12 (t, ^3J = 7.48 Hz, 2H, –$NC\mathbf{H}_2$), 2.41 (br, 4H, $C\mathbf{H}_{2COD}$), 1.90 (m, 4H, $C\mathbf{H}_{2COD}$), 1.68 (sext, ^3J = 7.42 Hz, 2H, $C\mathbf{H}_{2propyl}$), 0.84 (t, ^3J = 7.34 Hz, 3H, $C\mathbf{H}_{3propyl}$). δ_C (75 MHz, MeOD, 25 °C) (ppm)=165.7, 164.6, 132.5, 130.7, 130.4, 119.6, 117.8, 84.2 (br), 71.0 (br d, J = 13 Hz), 60.0, 30.5, 27.8, 26.1, 9.3. Analysis (calculated for $C_{18}H_{23}NNaO_4RhS$): C, 45.48; H, 4.88; N, 2.95; S, 6.75. Found: C, 45.57; H, 4.50; N, 3.18; S, 6.82%. ESI-MS (m/z) = 498.00 ($[M + Na]^+$, 84%).

Synthesis of 3-^{t}butyl-5-sulfonato propylsalicylaldimine rhodium(I)1,5-cyclooctadiene complex (8). Ligand (**4**) (0.044 g, 0.14 mmol), was dissolved in 10 cm^3 ethanol–DCM (1 : 1 volume) mixture. KOH (0.25 cm^3 of 1 M ethanol solution) was added and the reaction was stirred at room temperature for 30 minutes. $[Rh(COD)Cl]_2$ (0.035 g, 0.07 mmol) was added and the mixture stirred for 90 minutes. The reaction mixture was filtered by gravity and the solvent was removed to yield a yellow solid stuck to the sides of the round-bottomed flask. Diethyl ether was added and the product scratched off the walls of the flask, then filtered under vacuum. Yield of yellow solid (**8**) (0.045 g, 61%). mp.: decomp without melting, onset occurs at 277 °C. FT-IR (ν_{max}/cm^{-1}, KBr): 1607s (C=N). δ_H (400 MHz, DMSO-d_6, 25 °C) (ppm) = 8.20 (d, J = 1.79 Hz, 1H, $\mathbf{H}_{imine}$), 7.53 (d, ^4J = 2.32 Hz, 1H, **Ar**), 7.49 (d, ^4J = 2.29 Hz, 1H, **Ar**), 4.62 (br s, 2H, $C\mathbf{H}_{COD}$), 3.74 (br s, 2H, $C\mathbf{H}_{COD}$), 3.09 (t, ^3J = 7.59 Hz, 2H, –$NC\mathbf{H}_2$), 2.42 (br s, 4H, $C\mathbf{H}_{2COD}$), 1.86 (m, 4H, $C\mathbf{H}_{2COD}$), 1.63 (sext., ^3J = 7.56 Hz, 2H, $C\mathbf{H}_{2propyl}$), 1.29 (s, 9H, $C\mathbf{H}_3{}^t{}_{butyl}$), 0.87 (t, ^3J = 7.34 Hz, 3H, $C\mathbf{H}_{3propyl}$). δ_C (75 MHz, DMSO-d_6, 25 °C) (ppm)= 166.8, 164.0, 137.9, 134.1, 131.5, 128.8, 117.7, 83.0 (br), 71.4 (br), 60.0, 35.0, 29.9, 28.9, 27.2, 26.1, 11.5. Analysis (calculated for $C_{22}H_{31}NNaO_4RhS$): C, 49.72; H, 5.88; N, 2.64; S, 6.03. Found: C, 49.15; H, 5.53; N, 2.22; S, 6.48%. ESI-MS (m/z) = 508.1 ($[M - Na]^+$, 71%).

General procedure for the hydroformylation reactions

Hydroformylation reactions were carried out in a 90 ml stainless steel pipe reactor. The reactor was charged with toluene (5 ml) and water (5 ml) (1 : 1), 1-octene (715 mg, 6.37 mmol), *n*-decane as the internal standard (180 mg, 1.26 mmol) and either of the Rh catalyst precursors (**5** and **6**)/$[RhCl(COD)]_2$, or (**7** and **8**) (2.87×10^{-3} mmol, substrate : Rh ratio = 2220 : 1). The reactor was flushed three times with N_2 (g) then with syngas ($CO : H_2$, 1 : 1 ratio) followed by pressurizing and heating to the desired syngas pressure and temperature respectively. Samples were taken every 2 hours and analyzed using gas chromatography (GC). The products were confirmed in relation to authentic iso-octenes and aldehydes, alcohols and *n*-octane. For the catalyst recycling experiments, the organic layer was decanted, a fresh organic layer containing the substrate was introduced and the hydroformylation procedure was repeated.

Catalyst generation. Prior to hydroformylation reactions, (**5**)/$[RhCl(COD)]_2$ and (**6**)/$[RhCl(COD)]_2$ were generated by stirring ligands (**5** and **6**) separately in distilled water (5 ml) in the presence of aqueous KOH for 2 hours. The appropriate amount of $[RhCl(COD)]_2$ was then added and the solution was stirred at room temperature for 24 hours.

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