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Synthesis, characterisation and reactivity of water-soluble ferrocenylimine-Rh(I) complexes as aqueous-biphasic hydroformylation catalyst precursors

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ABSTRACT

Water-soluble complexes based on monosodium 5-sulfonato salicylaldimine (**3**) and 3-^{t}butyl-5-sulfonatosalicylaldimine have been synthesised *via* sulfonation and Schiff base condensation reactions. The ligand (**3**) and the new water-soluble mononuclear 5-sulfonatosalicylaldimine-ferrocenylimine complexes (**4** and **5**) have been synthesised and characterised fully using ^1H NMR, $^{13}C\{^1H\}$ NMR, and FT-IR spectroscopy, elemental analysis as well as mass spectrometry. Subsequently, the Rh(I) hetero-bimetallic complexes (**6** and **7**) were synthesised from $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) and the ferrocenylimine metalloligands (**4** and **5**) and characterised using various analytical and spectroscopic techniques. These complexes were applied as catalyst precursors in aqueous biphasic hydroformylation reactions. Optimal conditions were established at 95 °C (40 bar), showing the best chemoselectivity for aldehydes. The mononuclear ferrocenyl pre-catalysts (**4** and **5**) were inactive in the aqueous-biphasic hydroformylation of 1-octene. The heterobimetallic catalyst precursors (**6** and **7**) displayed good activity and could be recycled for at least 4 runs under the investigated conditions for the aqueous biphasic hydroformylation of 1-octene.

Introduction

The use of homogeneous catalysts which often display greater activity and selectivity, is often confounded by complications involving catalyst recovery and recycling. Various strategies have been developed in an effort to overcome the difficulties associated with the recovery of expensive and ever-diminishing transition metal resources. These strategies include supporting the catalyst on organic or inorganic supports or immobilising catalysts using biphasic media [1a–c], to name a few. The latter technique has been applied widely in hydroformylation reactions (the transition metal-catalysed reaction of olefins with hydrogen and carbon monoxide to afford aldehydes) as it strikes a “characteristic” balance of both heterogeneous and homogeneous processes [1a–f]. In biphasic media, the metal catalyst is heterogeneous with respect to the reactants, but the reaction (at an elevated temperature) occurs in a homogeneous environment. As such, on completion of a reaction, the catalyst remains in one phase and the product is in the other phase. These biphasic systems enable the catalyst to be reused without losing its superior homogeneous catalytic activity and selectivity as well as allowing for facile catalyst separation [1,2].

The Rührchemie/Rhône-Poulenc ‘Oxo’ process, is one of the first commercialised, industrial aqueous biphasic processes to use the hydroformylation reaction and now represents the most widely studied of the biphasic systems [2a–b]. This process uses a highly water-soluble TPPTS-modified Rh(I)-hydrido carbonyl complex and has grown to become the major synthetic route for the production of aldehydes, accounting for over 10 million tonnes per annum [3]. Rhodium-based metal complexes are generally preferred over other transition metals (Co, Ru, Ir, *etc.*) as hydroformylation catalysts due to the high activity and selectivity of the rhodium complexes under milder reaction conditions [4]. However, due to the greater expense of rhodium, novel strategies are required to ensure element sustainability. The aqueous-biphasic system is ideal as it utilises water, which is an eco- and user-friendly, relatively cheap, abundant and non-flammable solvent, in line with Green Chemistry Principles [3,5]. In addition, water is immiscible with most organic solvents, alleviating some of the challenges associated

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with homogeneous catalysis, such as long chain aldehyde product recovery. The aldehydes generated from the atom-economical hydroformylation reaction are typically processed into valuable consumer products in the cosmetics, bulk and fine chemicals industries [6].

Various avenues continue to be explored in order to improve and develop the aqueous-biphasic hydroformylation process. We have investigated the use of water-soluble Rh(I) complexes bearing chelating *N,O*-bidentate ligands, as well as metallodendrimers containing multiple peripheral active sites [7,8]. However, the multinuclear dendritic complexes do not show any improved catalytic activity from their mononuclear counterparts probably due to poor stability of the macromolecular structures in water [8]. Ligand modification is often of interest as, in some instances, it influences the main catalytic centre through changing electronic and steric factors, which in turn alters the hydroformylation rates and substrate conversion [7–11].

Recent efforts in the field of catalysis involve the use of bimetallic catalyst precursors in various olefin transformation reactions [12–16]. The improved catalytic properties of metalloenzymes (bearing two or more active centres) have catapulted studies into the application of bimetallic complexes in catalysis and medicine amongst other fields [17,18]. The premise behind this approach is that the addition of another metal confers unique and intriguing chemical and catalytic behaviour to the complexes and often results in improved activity and increased reaction rates [18]. A typical example may involve one metal acting as the main catalytic centre whereas the other metal serves as an electron reservoir, stabilising the electron density around the catalytic centre. Ferrocene, a redox-active sandwich complex, has been included in several heterobimetallic complexes in combination with other transition metals, bridged by various ligand structures. In this context, the inclusion of ferrocene moieties modified with phosphorus donor sites is very common [16,19,20].

To the best of our knowledge, no water-soluble ferrocenyl-based heterobimetallic complexes containing *N,O*-bidentate ligands have been reported in the literature. A combination of rhodium complexes with the chemically robust and redox- active ferrocene in forming water-soluble heterobimetallic complexes is of interest to the continued pursuit of designing and isolating new organometallic complexes with interesting properties. Moreover, the application of such complexes in the aqueous-organic biphasic hydroformylation of higher olefins, from an efficient catalyst design and Green Chemistry perspective, is also intriguing. As an extension of our previous work [8], we were prompted to evaluate the effect of heterobimetallic complexes in the hydroformylation process. In this paper, we report the synthesis and characterisation of a series of new water-soluble sulfonated heterobimetallic complexes and their reactivity as catalyst precursors in the aqueous biphasic hydroformylation of 1-octene.

Experimental

Materials and methods

All reactions were carried out in air unless otherwise stated. All solvents were reagent grade and used as received from Sigma–Aldrich, unless otherwise stated. $RhCl_3.3H_2O$ was purchased from Heraeus South Africa. All other chemicals were purchased from Sigma Aldrich and used as received. The sulfonated salicylaldehydes (**1** and **2**) were prepared according to previously reported literature procedures [8]. 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. Chemical shifts were reported in parts per million (ppm) 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 or 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 on a Waters Synapt G2 electron spray ionisation mass spectrometer in the positive or negative-ion mode. Elemental analyses were carried out using a Fision EA 110 CHNS Analyser. A Perkin Elmer Clarus 580 GC instrument equipped with a flame ionisation detector and 30 m capillary column was used for analysing and quantifying the catalytic products. Inductively coupled plasma optical emission spectroscopy experiments were conducted on an ICP-OES Varian 730-ES spectrophotometer.

Preparation of monosodium-5-sulfonatosalicylaldimine (*3*)

Hydrazine hydrate (0.805 g, 16.07 mmol) was added to a stirring solution of monosodium-5-sulfonato salicylaldehyde (1.80 g, 8.035 mmol) in ethanol and the reaction mixture refluxed for 1 h. The resultant pale yellow precipitate was collected by suction filtration while the solution was still hot, and washed with hot ethanol. Yield: (1.50 g, 78%). M.P.: decomposes without melting, onset occurs at 394 °C. ^{1}H NMR (DMSO-d$_6$, δ ppm): 11.51 (s, 1H, OH), 7.94 (s, 1H, H$_{imine}$), 7.48 (d, $^4J = 2.0$ Hz, 1H, Ar), 7.37 (dd, $^4J = 2.0$ Hz, $^3J = 8.4$ Hz, 1H, Ar), 6.88 (s, 2H, NH$_2$), 6.75 (d, ^3J = 8.4 Hz, 1H, Ar). ^{13}C{^{1}H} NMR (DMSO-d$_6$, δ ppm): 157.1, 141.9, 139.9, 126.9, 126.0, 119.0, 115.2. FT-IR (ν_{max}/cm^{-1}): 3409 (N–H), 3297 (O–H), 1619 (C=N). Anal. Calcd. For: $C_7H_7N_2NaO_4S$, C: 35.30, H: 2.96, N: 11.76. Found: C: 35.23, H: 2.70, N: 11.69. ESI-MS (*m/z*) = 215.01 ([M] where M is the anion).

Preparation of monosodium 5-sulfonatosalicylaldimine-ferrocenylimine (*4*)

Monosodium5-sulfonatosalicylaldimine (0.101 g, 0.4260 mmol) was added to a stirring solution of ferrocenecarboxaldehyde (9.10×10^{-2} g, 0.4260 mmol) in 20 cm^3 methanol and the reaction mixture refluxed for 48 h. The dark red solution was cooled to room temperature and filtered under gravity. The solvent of the filtrate was reduced to *ca.* 5 mL and dichloromethane was added to precipitate the product which was collected by filtration as a dark red solid. Yield: (0.151 g, 82%). M.P.: decomposes without melting, onset occurs at 174 °C. ^{1}H NMR (DMSO-d$_6$, δ ppm): 11.51 (s, 1H, OH), 8.82 (s, 1H, H$_{imine}$), 8.64 (s, 1H, H$_{imine}$), 7.91 (d, ^4J = 1.4 Hz, 1H, Ar), 7.59 (dd, ^3J = 8.4 Hz, ^4J = 1.6 Hz, 1H, Ar), 6.89 (d, ^3J = 8.4 Hz, 1H, Ar), 4.78 (br s, 2H, H$_{Fc}$), 4.57 (br s, 2H, H$_{Fc}$), 4.27 (s, 5H, H$_{Fc}$). ^{13}C{^{1}H} NMR (DMSO-d$_6$, δ ppm): 164.4, 160.9, 158.9, 140.6, 130.5, 128.7, 117.7, 115.9, 77.7, 71.8, 69.8, 69.4. FT-IR (ν_{max}/cm^{-1}): 1624 (C=N), 1589 (C=N). Anal. Calcd. For: $C_{18}H_{15}FeN_2NaO_4S.4H_2O$, C: 42.70, H: 4.58, N: 5.53. Found: C: 42.89, H: 4.44, N: 5.70. ESI-MS (*m/z*) = 411.01 ([M] where M is the anion). $S_{25\,^\circ C}$ = 1.87 mg mL^{-1} in water.

Preparation of 3-^{t}butyl-5-sulfonato salicylaldimine-ferrocenylimine complex (*5*)

Hydrazine hydrate (0.187 g, 3.729 mmol) was added dropwise to a stirring solution of 3-^{t}butyl-5-sulfonatosalicylaldehyde (1.05 g, 3.729 mmol) in methanol and the reaction heated for 6 h at 45 °C. Ferrocenecarboxaldehyde (0.799 g, 3.731 mmol) was then added and the reaction mixture heated at 45 °C for 24 h. The dark brown solution was filtered by gravity to remove an orange precipitate, the ferrocenylcarbaldehyde hydrazone (see supplementary material for characterisation data). The volume of the filtrate was then reduced to *ca.* 5 mL and diethyl ether was added to precipitate out a brown solid which was collected by filtration and dried *in vacuo*. Yield: (1.50 g, 82%). M.P.: decomposes without melting, onset occurs at

248 °C. ^{1}H NMR (DMSO-d$_6$, δ ppm): 12.82 (s, 1H, OH), 8.82 (s, 1H, H$_{imine}$), 8.68 (s, 1H, H$_{imine}$), 7.68 (d, $^4J = 2.25$ Hz, 1H, Ar), 7.63 (d, $^4J = 2.25$ Hz, 1H, Ar), 4.78 (br s, 2H, H$_{Fc}$), 4.58 (br s, 2H, H$_{Fc}$), 4.28 (s, 5H, H$_{Fc}$), 1.42 (s, 9H, CH3 ^{t}$_{butyl}$). ^{13}C{^{1}H} NMR (DMSO-d$_6$, δ ppm): 164.1, 162.7, 157.9, 138.9, 135.2, 127.7, 126.8, 116.3, 76.74, 71.17, 69.07, 68.67, 34.22, 28.88. FT-IR (ν_{max}/cm^{-1}): 3390 (O—H), 1615 (C=N), 1590 (C=N). Anal. Calcd. For: $C_{22}H_{23}FeN_2NaO_4S.6.5H_2O$, C: 43.50, H: 5.97, N: 4.61. Found: C: 43.62, H: 5.12, N: 4.39. ESI-MS (*m/z*) = 467.07 ([M] where M is the anion). $S_{25\,^\circ C} = 4$ mg mL^{-1} in water.

*Preparation of monosodium 5-sulfonatosalicylaldimine ferrocenylimine rhodium(I)1,5-cyclooctadiene heterobimetallic complex (**6**)*

Monosodium 5-sulfonatosalicylaldimine-ferrocenylimine (0.100 g, 0.2310 mmol) and sodium hydride (6.00 × 10^{-3} g, 0.2310 mmol) were stirred together in dichloromethane for 90 min. [Rh(COD)Cl]$_2$ (5.70 × 10^{-2} g, 0.1155 mmol) was added and the reaction mixture stirred for 16 h. Methanol was added to quench the NaH and the solution was filtered by gravity. The solvent was removed to afford an orange solid. Yield: (0.140 g, 94.2%). M.P.: decomposes without melting, onset occurs at 263 °C. ^{1}H NMR (DMSO-d$_6$, δ ppm): 8.03 (s, 1H, H$_{imine}$), 7.97 (s, 1H, H$_{imine}$), 7.70 (d, $^4J = 2.2$ Hz, 1H, Ar), 7.50 (dd, $^3J = 8.8$ Hz, $^4J = 2.1$ Hz, 1H, Ar), 6.61 (d, $^3J = 8.7$ Hz, 1H, Ar), 4.57 (br s, 2H, H$_{Fc}$), 4.54 (br s, 2H, H$_{Fc}$), 4.33 (m, 9H, H$_{Fc}$ + CH$_{COD}$), 2.42 (m, 4H, CH$_{2,\ COD}$), 1.90 (m, 4H, CH$_{2,\ COD}$). ^{13}C {^{1}H} NMR (DMSO-d$_6$, δ ppm): 165.8, 158.7, 153.4, 135.2, 132.6, 132.2, 120.2, 115.9, 77.4, 71.4, 69.8, 69.0, 30.3. FT-IR (ν_{max}/cm^{-1}): 1600 (C=N). Anal. Calcd. For: $C_{26}H_{26}FeN_2NaO_4R_{hS}.4CH_2Cl_2$, C: 36.62, H: 3.48, N: 2.85. Found: C, 36.99; H, 3.90; N, 2.67. ESI-MS (*m/z*) = 411.01 ([M−Rh(COD)] where M is the anion). $S_{25\,^\circ C} = 16.7$ mg mL^{-1} in water.

*Preparation of monosodium 3-^{t}butyl-5-sulfonato salicylaldimine-ferrocenylimine rhodium(I)1,5-cyclooctadiene heterobimetallic complex (**7**)*

3-^{t}butyl-5-sulfonatosalicylaldimine-ferrocenylimine (0.102 g, 0.2072 mmol) and sodium hydride (5.00 × 10^{-3} g, 0.2105 mmol) were stirred together in dichloromethane at room temperature for 90 min. [Rh(COD)Cl]$_2$ (5.11 × 10^{-2} g, 0.1036 mmol) was added and the reaction mixture stirred for 24 h. Methanol was added to quench the NaH and the solution was filtered by gravity. The solvent was then reduced to *ca.* 5 mL and diethyl ether was added to precipitate out a brown solid product. The compound was collected by suction filtration and then dried *in vacuo*. Yield: (0.140 g, 97%). M.P.: decomposes without melting, onset occurs at 335 °C. ^{1}H NMR (DMSO-d$_6$, δ ppm): 8.03 (s, 1H, H$_{imine}$), 7.94 (s, 1H, H$_{imine}$), 7.56 (s, 1H, Ar), 7.54 (s, 1H, Ar), 4.65 (br s, 2H, H$_{Fc}$), 4.52 (br s, 2H, H$_{Fc}$), 4.31 (m, 9H, H$_{Fc}$ + CH$_{COD}$), 2.42 (m, 4H, CH$_{2,\ COD}$), 1.90 (m, 4H, CH$_{2,\ COD}$), 1.31 (s, 9H, CH$^t_{3butyl}$). ^{13}C{^{1}H} NMR (DMSO-d$_6$, δ ppm): 164.0, 158.3, 153.5, 137.8, 133.6, 130.5, 128.1, 115.7, 76.95, 70.86, 69.26, 68.44, 34.65, 29.49. FT-IR (ν_{max}/cm^{-1}): 1592 (C=N). Anal. Calcd. For: $C_{30}H_{34}FeN_2NaO_4RhS.4CH_2Cl_2$, C: 39.26, H: 4.07, N: 2.69. Found: C: 39.08, H: 4.64, N: 2.65. ESI-MS (*m/z*) = 467.07 ([M− Rh(COD)] where M is the anion). Sparingly soluble in water.

General procedure for the catalytic experiments

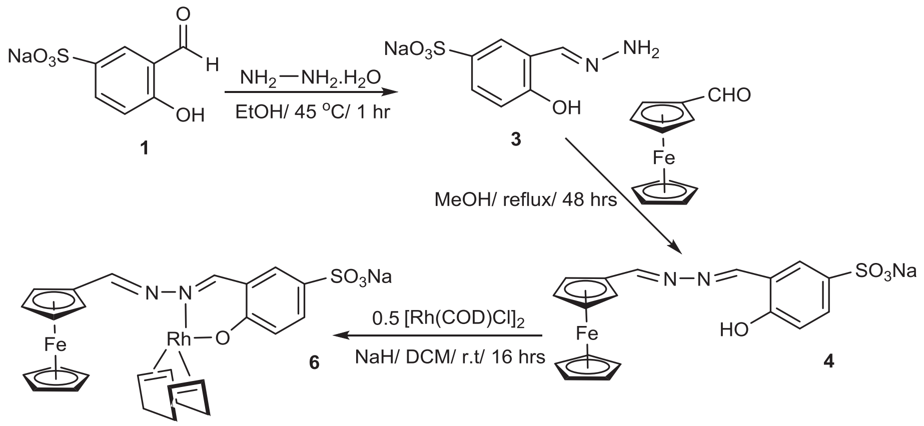
In a typical experiment, the catalyst precursor (**4**–**7**) (2.87 × 10^{-3} mmol) was dissolved in distilled water (5 cm^3) and transferred into a stainless steel pipe reactor (90 ml). The substrate, 1-octene, (805 mg, 7.175 mmol)} and the internal standard, n-decane, (204 mg, 1.435 mmol)} were dissolved in toluene (5 ml) and then added into the reactor. The air-tight reactor was then deaerated by flushing three times with N$_2$ gas, twice with syngas then charged with syngas (1:1, CO:H$_2$ ratio) and heated to the desired temperature and pressure. After the reaction time, the reactor was depressurised and the reaction mixture transferred into a vial for cooling to 0 °C. The organic layer was then decanted and a sample analysed by gas chromatography. For the recycling studies, a fresh toluene layer containing the substrate and the internal standard was introduced in the reactor and the catalytic reaction repeated.

Results and discussion

*Synthesis and characterisation of the ligands (**1**–**3**)*

The sulfonated ligands **1** (Scheme 1) and **2** (Scheme 2) were readily synthesised as previously described in literature by the reaction of the commercially available salicylaldehydes with aniline [8]. This was achieved through a series of aldehyde group protection, sulfonation and acid-catalysed imine hydrolysis reactions. The ligands **1** and **2** were isolated in good yields (62% and 72.5%, respectively) and characterised fully using various analytical and spectroscopic techniques.

The new hydrazone-based monosodium 5-sulfonatosalicylaldimine ligand **3** was prepared by the Schiff-base condensation reaction of hydrazine monohydrate with monosodium 5-sulfonatosalicylaldehyde **1** in dry ethanol (Scheme 1) and was isolated in good yield as a pale yellow solid. The ligand is soluble in water, methanol and dimethyl sulfoxide and was characterised



Scheme 1. Outline of the preparation of the sulfonated mononuclear (4) and heteronuclear (6) complexes.

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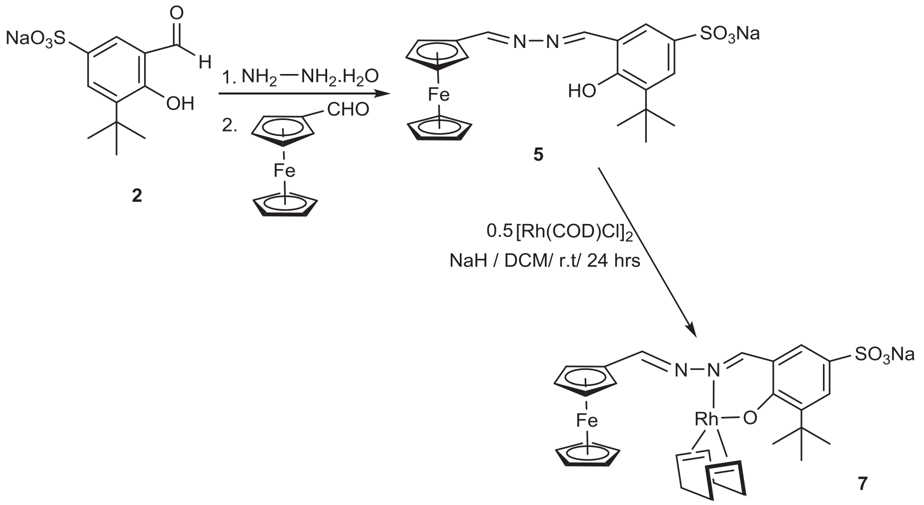

Scheme 2. Outline of the preparation of the t-butyl-substituted sulfonated mononuclear (**5**) and heteronuclear (**7**) complexes.

by elemental analysis (C, H, N), FT-IR, ^1H NMR and $^{13}C\{^1H\}$ NMR spectroscopy as well mass spectrometry. Both the ^1H NMR and $^{13}C\{^1H\}$ NMR spectra show the formation of the imine functionality through signals at $\delta = 7.94$ (^1H) and *ca.* $\delta = 140$ ($^{13}C\{^1H\}$), with all the aromatic protons observed in the usual region (at $\delta = 7.48$, 7.37 and 6.75) and carbon signals occurring in their characteristic regions.

The infrared spectrum of ligand **3** further confirms the presence of the hydrazone moiety as there is no aldehyde $\nu(C{=}O)$ absorption band, and the spectrum shows a characteristic strong imine $\nu(C{=}N)$ stretching frequency at 1619 cm^{-1}. The observed shift from high frequency for $\nu(C{=}O)$ to lower frequency for $\nu(C{=}N)$ is due to the weakening of the double bond character as a result of a reduced dipole moment emanating from the difference in electronegativity from oxygen (3.5) to nitrogen (2.5) [21]. Also observed in the FT-IR spectrum are absorption bands at 3409 cm^{-1} and 3293 cm^{-1} corresponding to $\nu(N–H)$ and $\nu(O–H)$ stretching frequencies respectively. ESI mass spectrometry in the negative mode corroborates the formation of this ligand by displaying a base peak for the $[M]^-$ ion at $m/z = 215.01$, where M is the anion.

*Synthesis of the sulfonated ferrocenylimine mononuclear complexes (**4** and **5**)*

The mononuclear complex **4** was synthesised by the Schiff-base condensation reaction of ferrocenecarboxaldehyde with monosodium 5-sulfonatosalicylaldimine (**3**) and was isolated as a dark red solid in good yield (82%), (Scheme 1). The mononuclear complex (**5**) was successfully prepared through a one-pot synthesis by the Schiff-base condensation reaction of monosodium 3-^{t}butyl-5-sulfonatosalicylaldehyde (**2**) with hydrazine monohydrate and ferrocenecarboxaldehyde (Scheme 2). Complex (**5**) was isolated as a dark brown solid in good yield (82%), with the ferrocenylcarbaldehyde hydrazone as a by-product. Both complexes (**4** and **5**) are new and have shown good solubility in water (1.82 mg/mL and 4 mg/mL, respectively). These complexes were characterised fully by elemental analysis (C, H, N and S), FT-IR, ^1H NMR and $^{13}C\{^1H\}$ NMR spectroscopy as well as mass spectrometry.

The infrared spectrum for each complex shows the presence of the imine groups as strong and broad $\nu(C{=}N)$ bands, each with a shoulder assigned to the second imine. The ^1H NMR spectra of the complexes show the presence of two imine proton peaks as singlets at $\delta = 8.82$ and 8.64 ppm for **4** and $\delta = 8.82$ and 8.68 ppm for **5**. The aromatic protons are observed in their characteristic region at $\delta = 7.91$, 7.59 and 6.89 ppm for complex **4**, and $\delta = 7.68$ and 7.63 ppm for complex **5**. The protons of the unsubstituted cyclopentadienyl ring of the ferrocenyl moiety are observed as broad singlets at *ca.* δ 4.3 in the ^1H NMR spectra of the complexes. The monosubstituted cyclopentadienyl ring protons are observed as broadened signals. Typically, these protons resonate as a doublet or triplet but these cannot be observed on the given NMR timescale and these protons average out to one broadened signal over the same chemical shift. The mass spectral data in the negative mode is consistent with the proposed structures of the complexes by displaying base peaks for $[M]^-$ ions at $m/z = 411.01$ and 467.07, corresponding to the molecular weights of the anions of **4** and **5** respectively.

*Synthesis of the sulfonated ferrocenylimine-Rh(I) heterobimetallic complexes (**6** and **7**)*

The new heterobimetallic complexes (**6** and **7**) were synthesised by reacting the mononuclear complexes **4** (Scheme 1) and **5** (Scheme 2) with the Rh(I) precursor $[Rh(COD)Cl]_2$, (COD = 1,5-cyclooctadiene). The complexes were obtained in good yields (94%–97%). The heterobimetallic complex **7** is less soluble in water than its analogous complex **6**, probably due to the greater hydrophobic nature of the tertiary butyl substituent. Deprotonation in the presence of sodium hydride, followed by coordination of the rhodium metal for complex **6**, is confirmed by the ^1H NMR spectrum, which no longer displays a signal corresponding to the hydroxyl proton. An upfield shift of the imine protons of **4** from 8.82 and 8.64 ppm to 8.03 and 7.97 ppm in **6** is observed in the ^1H NMR spectra, further confirming the coordination of the metal. The shift may be attributed to back-donation of electrons from the rhodium metal to the imine nitrogen, therefore creating increased electron density in the imine functionality and consequently exerting shielding effects on the imine protons. The olefinic COD protons are observed as overlapping signals in the same region as the protons in the unsubstituted ferrocenyl moiety (at *ca.* $\delta = 4$). Though not observed in this particular spectrum, in some instances, the olefinic COD protons are observed as separate signals in the proton spectrum, which may be attributed to the asymmetric environment induced by the chelating *N*,*O*-bidentate ligand. The splitting of the signals for these protons may be due to the trans effects of the coordinating N,O-bidentate ligand, which is also observed in

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related compounds [22]. The exo- and endo-methylene protons of the COD ($\delta = 2.4$ and 1.9 ppm) are observed further upfield as two multiplets. This behaviour is also observed for complex **7**.

The $^{13}C\{^{1}H\}$ NMR spectra, together with 2D-NMR experiments (HSQC), support the formation of the heterobimetallic complex **6**. The carbon adjacent to the coordinating oxygen ($\delta = 165.8$) initially observed in **4** at $\delta = 158.9$ ppm, is observed to have shifted downfield. This is attributed to the increased deshielding effect exerted by the adjacent oxygen atom as a result of coordination to the rhodium metal center. Infrared spectroscopy of complex **6** indicates a strong sharp band at 1600 cm^{-1} assigned to the ν(C=N) stretching frequency of the coordinating imine, with a shoulder presumably representing the free non-coordinating imine. The frequency shift of the imine absorption band from complex **4** to complex **6** (1624 to 1600 cm^{-1}) substantiates coordination of the rhodium metal centre to the imine nitrogen. This is due to sigma donation from the nitrogen and subsequent back-donation of electrons from the rhodium metal through synergic effects. As a result, the Rh–N bond strengthens whereas the C=N bond weakens. This decreases the wavenumber of the C=N bond in the infrared spectrum as observed in the infrared spectrum of **6**. Such shifts have also been reported for similar compounds in the literature [7,8]. Similar shifts are also observed on going from complex 5 to 7.

Aqueous biphasic hydroformylation of 1-octene

The reactivity of complexes (**4**–**7**) as catalyst precursors was evaluated in the aqueous–organic biphasic hydroformylation of 1-octene. Reactions of this study were based on the previously reported conditions of the hydroformylation of 1-octene using analogous Rh(I) catalyst precursors containing *N,O*-bidentate ligands [8]. In our hands, the mononuclear ferrocenylimine complexes (**4** and **5**) (containing no rhodium) were inactive in the hydroformylation reactions under these conditions. Examples of rhodium complexes with ferrocene-based donors as catalyst precursors in the hydroformylation of olefins have been reported in the literature [12,15]. However, there have been no reports of water-soluble ferrocenyl–Rh(I) heterobimetallic catalyst precursors containing *N,O*-bidentate ligands used for the hydroformylation of olefins.

*Reactivity of **6** and **7** as hydroformylation catalyst precursors*

The water-soluble ferrocenylimine–Rh(I) heterobimetallic catalyst precursors (**6** or **7**) were dissolved in distilled water (5 mL) at a catalyst loading of 2.87×10^{-3} mmol and charged into stainless steel pipe reactors for the aqueous biphasic hydroformylation of 1-octene. Under conditions of 40 bar and 95 °C, the catalyst precursor **6** displayed excellent conversion (99%) of 1-octene as well as excellent chemoselectivity (99%) towards aldehydes (Table 1, Entry 1). Catalyst precursor **7** also showed excellent conversion (95%) and good chemoselectivity towards aldehydes (76%) (Table 1, Entry 2).

Isomerisation of 1-octene is observed with this catalyst precursor under the optimum conditions. Furthermore, the presence of the electron-donating ^{t}Bu substituent in catalyst precursor 7 seems to lower the chemoselectivity, yet improves the regioselectivity towards linear aldehydes. Good activity was observed for both catalyst precursors (**6**, >300 h^{-1}) and (**7**, >200 h^{-1}). The improved regioselectivity towards linear aldehydes in catalyst **7** is expected due to the greater steric constraints imposed by the bulkier catalyst. This is similar to the data observed for related ^{t}Bu substituted catalysts containing *N,O*-bidentate ligands reported by Matsinha and co-workers [7].

Recyclability studies

The catalyst precursor **6** could be recycled for at least 5 cycles with a gradual loss in activity and 1-octene conversion (Fig. 1). Catalyst precursor **7** could be recycled 4 times with a slight decease in conversion before any loss in catalytic activity was observed. The observed steady decrease in activity and 1-octene conversion can be ascribed to partial agglomeration of nanoparticles observed in the aqueous layer and which was attested to through mercury poisoning tests. Leaching of the catalyst from the aqueous layer into the organic layer was also noted (vide infra), shown by the discolouration of the aqueous layer with each recycling.

The catalyst precursor **6** showed consistently good chemoselectivity towards aldehydes through several cycles in comparison with the substituted analogue **7**. Both complexes **6** and **7** show comparable catalytic activity and selectivity to the previous work done in our group [8]. Catalyst precursor **7** showed better regioselectivity towards linear aldehydes than **6** (Fig. 2(a) and (b)). This would be expected as the bulkier groups on the catalysts would favour linear products in the hydroformylation reactions. The observed regioselectivity towards branched aldehydes for the first run of catalyst **6** suggests that the flexibility of the ligand promotes isomerisation of 1-octene well before hydroformylation could occur. Such effects of the ligand flexibility are not observed with catalyst precursor **7**, as the ^{t}Bu substituent imparts the bulkiness required to favour linear products. An average linear to branched aldehyde ratio of 60:40 is realised for both catalyst precursors. The

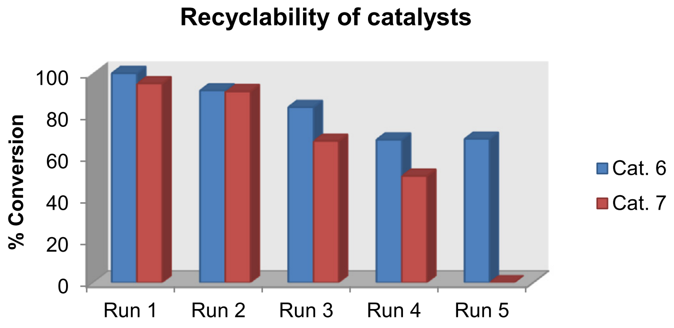

Fig. 1. Conversion of 1-octene in recyclability studies, performed in a 90 ml stainless steel pipe reactor. Solvent (1:1, toluene:water), substrate (1-octene, 7.175 mmol), internal standard (n-decane, 1.435 mmol), metal catalyst (Rh, 2.87×10^{-3} mmol), syngas (1:1, CO:H_2), reaction time (8 h).

Table 1
Hydroformylation of 1-octene with catalyst precursors **6** and **7** at 8 h.

Entry	Complex	Conv. (%)	Aldehydes (%)			Isooctenes (%)	*n*/*iso*	TOF (h^{-1})
			Total aldehydes	Nonanal	Branched			
1	**6**	99	99	39	61	0	0.64	313
2	**7**	95	76	55	45	24	1.2	229

Reactions carried out with (CO:H_2) (1:1) at 40 bar, 95 °C in distilled water (5 mL) with 7.175 mmol of 1-octene and 2.87×10^{-3} mmol Rh catalyst. GC conversions obtained using *n*-decane as an internal standard in relation to authentic standard iso-octenes and aldehydes. TOF = (mol product/mol cat.) h^{-1} and is based on total aldehydes produced.

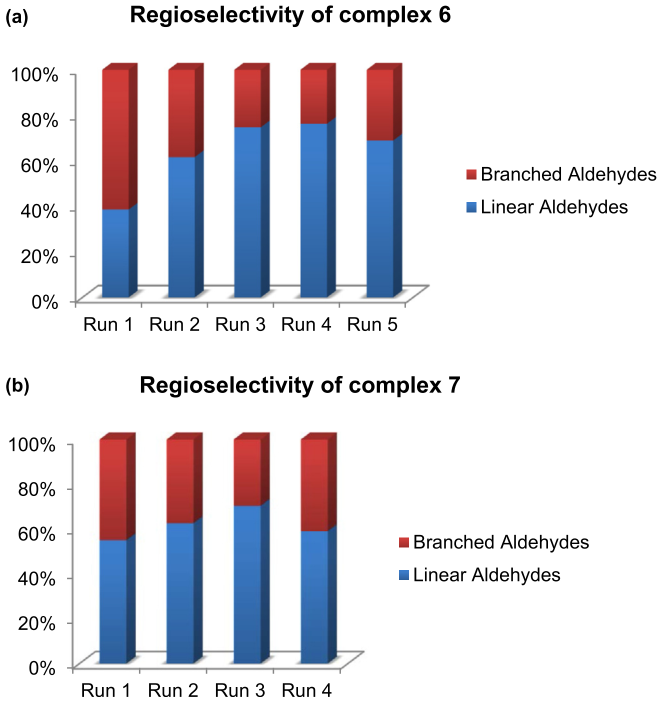

Fig. 2. Regioselectivity of the catalysts in recyclability studies performed in a 90 ml stainless steel pipe reactor. Solvent (1:1, toluene:water), substrate (1-octene, 7.175 mmol), internal standard (n-decane, 1.435 mmol), metal catalyst (Rh, 2.87 × 10^{-3} mmol), syngas (1:1, CO:H_2), reaction time (8 h).

observed regioselectivity is consistent with literature for related substituted *N,O*-bidentate ligands [7,8].

Phosphine modified ligands in heterobimetallic complexes of ferrocene and rhodium have been reported to show improved catalytic activity compared to their mononuclear counterparts in the hydroformylation of olefins [19,20]. The heterobimetallic catalyst precursors bearing *N,O*-bidentate ligands in this study showed diminished activity in comparison to previous studies.

Leaching studies

The aqueous layer of each complex (**6** and **7**) was analysed for the rhodium metal using inductively coupled plasma optical emission spectrometry (ICP-OES). The catalysts show poor conversions after the fifth and fourth cycle for compounds **6** and **7** respectively, with almost a 90% loss of metal observed. This substantiates the observed decrease in catalytic activity and 1-octene conversion during recyclability studies, particularly after the fifth recycling run. Furthermore, the observed 1-octene conversion may be due to a combination of the actual homogeneous active catalyst and catalysis mediated by rhodium nanoparticles.

Conclusions

A series of new water-soluble *N,O*-bidentate ligands based on sulfonato-salicylaldimine entities and containing ferrocene was synthesised. These compounds were coordinated to rhodium(I) to produce new water-soluble ferrocenylimine-Rh(I) heterobimetallic complexes. All the complexes were obtained in good yields and characterised using various spectroscopic and analytical techniques. The new water-soluble mono- and heteronuclear complexes were evaluated as catalyst precursors in the aqueous biphasic hydroformylation of 1-octene. The ferrocenyl mononuclear complexes were inactive in the hydroformylation studies. The heterobimetallic catalyst precursors show moderate activity and recyclability for at least four cycles with a significant loss in activity and conversion of 1-octene after the fourth cycle. The presence of the bulky ^{t}Bu-substituent favours the production of linear aldehydes due to the increased steric crowding around the active metal centre. However, the presence of the ferrocene moiety does not seem to have a significant catalytic influence over the previously reported water-soluble Rh(I) monomeric catalyst precursors. A small amount of black particulate matter was also observed signifying catalysis by the homogeneous precursors and mediated by nanoparticles. Leaching of the catalyst from the aqueous layer to the organic layer was very pronounced, particularly after the fourth recycle.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.04.029.

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