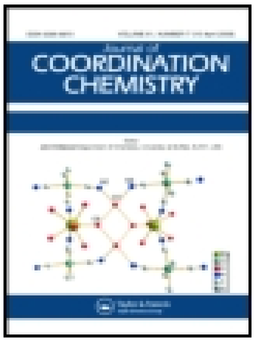

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Leah C. Matsinha & Banothile C. E. Makhubela

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Synthesis, characterization and evaluation of heterobimetallic Fe(II)/Rh(I) and Fe(II)/Ru(II) complexes as catalyst precursors for hydroformylation of 1-octene

LEAH C. MATSINHA and BANOTHILE C. E. MAKHUBELA*

Department of Chemistry, University of Johannesburg, PO Box 524, Auckland Park, 2006, South Africa

Two new ferrocenyl iminopyridyl ligands, L1 and L2, have been synthesized and characterized using spectroscopic and analytical techniques. Both ligands were used to prepare new Rh(I) and Ru(II) ferrocenyl complexes **1**-**4**. The structures of the complexes were confirmed using ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy, high resolution electrospray ionization mass spectrometry and infrared spectroscopy. The complexes were tested as catalysts in the hydroformylation of 1-octene. Rh ferrocenyl complexes **1** and **4** produced aldehydes under mild conditions while the Ru-ferrocenyl complexes **2** and **3** required higher temperature and pressure for effective hydroformylation to occur. The catalysts display excellent aldehyde chemoselectivity with varying regeoselectivity depending on temperature and pressure conditions employed. At high temperatures, the Rh ferrocenyl precatalysts favor formation of branched aldehydes due to increased isomerization at high temperatures. The Ru ferrocenyl precatalysts displayed less hydroformylation activity however the complexes show good chemoselectivity for aldehydes with no hydrogenation products formed.

Keywords: Hydroformylation; Rhodium-catalyzed; Ruthenium-catalyzed; Ferrocenylimine; Heterobimetallic complexes; 1-Octene

1. Introduction

Hydroformylation is an important reaction that provides direct access to aldehydes from alkenes [1-4]. Apart from aldehydes, alcohol products can also be formed and these together with aldehydes can be industrially converted into solvents, coatings and plasticizers [1, 5-8]. Various transition metals such as Co, Rh, Ru, Ir and Pd have been used as catalysts for this reaction [1, 9, 10]. However, Rh catalyzed hydroformylation reactions have been extensively studied due to the high activity of Rh [6, 11-17]. The hydroformylation reaction is traditionally performed

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*Corresponding author. Email: bmakhubela@uj.ac.a

using pressured syngas (CO/H_2), however the use of CO_2 as a carbon source is becoming popular due to the increasing CO_2 levels in the atmosphere [18]. In some cases, instead of H_2, reports on the use of formic acid as a hydrogen source have also been published [2].

The incorporation of a second metal such as Fe in heterobimetallic systems has been found to be of benefit during catalysis [19-25]. In certain instances, bimetallic systems are more active than their mononuclear analogues with the same structure at the metal center. This increase in catalytic activity is usually attributed to a cooperative interaction between the two metal centers [26]. A combination of ferrocene and Rh has been previously investigated in the aqueous biphasic hydroformylation of 1-octene [14, 25]. These heterobimetallic systems displayed good activity and could be easily recovered for recycling. This combination of Rh and ferrocene is of interest in the discovery of highly active and selective homogeneous hydroformylation catalysts.

Herein we describe the synthesis and characterization of heterobimetallic organometallic complexes and the investigation of the catalytic activity of these complexes as 1-octene hydroformylation catalyst precursors using 1:1 CO/H_2.

2. Experimental

2.1. *Materials and methods*

All compounds were prepared using standard Schlenk and vacuum line techniques. 2-Picolylamine, 2-amino pyridine, chloroform-d and dimethyl sulfoxide–d_6 were purchased from Sigma-Aldrich. The dimeric metal precursors $[RuCl_2(p\text{-cymene})]_2$ [27] and $[RhCl(COD)]_2$ [28] were prepared according to previously reported methods. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Ultrashield 400 MHz (^1H: 400 MHz; ^{13}C: 100 MHz) spectrometer. Spectrometer values were reported relative to the internal standard tetramethylsilane (δ 0:00). All chemical shifts were reported in ppm. FT-IR spectra were recorded using a Perkin Elmer FT-IR Spectrum BX II fitted with an ATR probe. Melting points were obtained using a Gallenkamp Digital Melting-point Apparatus 5A 6797. Elemental analysis was performed on a Thermo Scientific FLASH 2000 CHNS-O Analyzer. Mass spectrometry was carried out on a Waters API Quattro Micro Triple Quadrupole electrospray ionization mass spectrometer. Data were recorded in the positive ion-mode. Hydroformylation samples were analyzed on a Scion 456-GC with 30 m × 0.25 mm cyanopropylphenylmethylpolysiloxane phase column. Electrochemical studies were carried out with a Bio-logic SP-200 potentiostat connected to a data controller. A three-electrode system was used in the experiment with a glassy carbon electrode (GCE) as the working electrode. Ag/AgCl electrode (saturated KCl) and a Pt-electrode were used as the reference and counter electrodes, respectively.

2.2. *Synthesis and characterization of L1*

Acetyl ferrocene (0.558 g, 2.40 mmol) was dissolved in 20 ml ethanol. To this was added a few drops of formic acid followed by addition of 2-amino pyridine (0.230 g, 2.40 mmol) in 20 ml ethanol. This was left to reflux for 16 h and the solvent was reduced to about 5 ml. The mixture was cooled to 0 °C and the brown solid formed was recovered by vacuum filtration using a Hirsch funnel. The solid was dried under vacuum to afford a brown solid. Yield (0.663 g, 91%). Melting Point: 144 °C - 146 °C. FT-IR (ν_{max}/cm^{-1}, 1655 (C=N$_{imine}$), 1581 (C=N$_{pyridyl}$). ^{1}H NMR: CDCl$_3$, δ (ppm): 8.45 (s, 1H, H$_{pyr}$), 7.95 (s, 1H, H$_{pyr}$), 7.81 (t, ^{3}J = 8.4 Hz, 1H, H$_{pyr}$), 6.62 (d, ^{3}J = 5.6 Hz, 1H, H$_{pyr}$), 4.74 (s, 2 H, H$_{ferrocene}$), 4.47 (s, 2H, H$_{ferrocene}$), 4.18 (s, 5H, H$_{ferrocene}$), 2.37 (s, 3H, H$_{methyl}$). ^{13}C{^{1}H} NMR: CDCl$_3$, δ (ppm): 168.5, 157.1, 141.5, 140.5, 112.7, 111.3, 79.3, 72.4, 69.9, 67.9, 27.4. Elemental Anal. Calculated for $C_{17}H_{16}FeN_2$ (%): C, 67.13; H, 5.30; N, 9.21. Found: C, 67.29; H, 5.35; N, 9.49. HR-ESI-MS: *m/z* = 327.1714 for [M+Na]$^+$. E$_{pa}$ = 0.35 eV, E$_{pa}$ = 0.57 eV; E$_{pc}$ = 0.43 eV.

2.3. *Synthesis and characterization of L2*

Acetyl ferrocene (0.0570 g, 0.250 mmol) in 20 ml dichloromethane was added to a solution of 2-picolylamine (0.0800 g, 0.250 mmol) in 20 ml dichloromethane. The resulting solution was refluxed for 24 h. The solvent was reduced to about 5 mL and excess diethyl ether was added to precipitate an orange solid. This was filtered using a Buchner funnel, washed with diethyl ether and dried under vaccum to afford an orange solid as the desired product. Yield (0.060 g, 75%). Melting Point: Decomposes without melting at 162 °C. FT-IR (ν_{max}/cm^{-1}, 1640 (C=N$_{imine}$), 1594 (C=N$_{pyridyl}$). ^{1}H NMR: CDCl$_3$, δ (ppm): 8.52 (s, 1H, H$_{pyr}$), 7.61 (t, ^{3}J = 10.2 Hz, H$_{pyr}$), 7.25 (s, 1H, H$_{pyr}$), 7.12 (t, ^{3}J = 11.6 Hz, H$_{pyr}$), 4.74 (s, 2H, H$_{ferrocene}$), 4.47 (s, 2H, H$_{ferrocene}$), 4.17 (s, 5H, H$_{ferrocene}$), 2.36 (s, 3H, H$_{methyl}$), 1.88 (s, 2H, H$_{ethyl}$). ^{13}C{^{1}H} NMR: CDCl$_3$, δ (ppm): 160.5, 148.3, 146.9, 137.9, 79.8, 72.6, 69.8, 67.1, 66.9, 61.8, 32.4, 30.8. Elemental Anal. Calc. for $C_{18}H_{18}FeN_2$

(%): C, 67.94; H, 5.70; N, 8.80. Found: C, 68.00; H, 5.49; N, 8.32. HR-ESI-MS: *m/z* = 318.0898 for $[M+H]^+$. E_{pa} = 0.36 eV, E_{pa} = 0.58 eV; E_{pc} = 0.40 eV.

2.4. *Synthesis and characterization of Rh-ferrocenyl complex 1*

The rhodium precursor $[RhCl(COD)]_2$ (0.168 g, 0.341 mmol) was dissolved in 20 ml of dichloromethane and this was added to a stirring solution of ferrocenyl ligand L1 (0.209 g, 0.682 mmol) in 20 ml dichloromethane. This was left to stir at room temperature for 16 h. The mixture was filtered by gravity and the solvent was removed under reduced pressure to afford an orange solid which was dried under vacuum to afford the desired product. Yield (0.253 g, 63%). Melting Point: Decomposes without melting at 162 °C. FT-IR (ν_{max}/cm^{-1}, 1655 ($C{=}N_{imine}$), 1622 ($C{=}N_{pyridyl}$). ^1H NMR: $CDCl_3$, δ (ppm): 7.93 (br s, 1H, H_{pyr}), 7.35 (t, ^3J = 8.2 Hz, 1H, H_{pyr}), 7.46 (d, ^3J = 7.2 Hz, 1H, H_{pyr}), 6.11 (s, 1H, H_{pyr}), 4.76 (s, 2H, $H_{ferrocene}$), 4.54 (s, 2H, $H_{ferrocene}$), 4.35 (s, 4H, H_{COD}), 4.34 (s, 5H, $H_{ferrocene}$), 2.42 (s, 3H, H_{COD}), 2.33 (s, 3H, H_{methyl}) 1.93 (m, 4H, H_{COD}). $^{13}C\{^1H\}$ NMR: $CDCl_3$, δ (ppm): 160.5, 148.3, 146.9, 137.9, 129.9, 81.2, 79.8, 72.6, 69.8, 67.1, 66.9, 61.8, 32.4, 30.8. Elemental Anal. Calc. for $C_{27}H_{36}ClFeN_2Rh$ (%): C, 52.45; H, 5.87; N, 4.53. Found: C, 52.41; H, 5.83; N, 4.50. HR-ESI-MS: *m/z* = 551.0173 for $[M+H]^+$. E_{pa} = 0.58 eV, 0.42 eV; E_{pc} = 0.43 eV, E_{pc} = 0.35 eV.

2.5. *Synthesis and characterization of Ru-ferrocenyl complex 2*

The ruthenium precursor $[RuCl_2(p\text{-cymene})]_2$ (0.142 g, 0.232 mmol) was dissolved in 20 mL dichloromethane. To it was added L1 dropwise (0.142 g, 0.463 mmol), dissolved in 20 mL dichloromethane. The solution was left to stir at room temperature for 16 h. The solvent was removed under reduced pressure and the solid was washed with diethyl ether and dried under vacuum to afford the desired product as a dark brown solid. Yield (0.0681 g, 26%). Melting Point: 164 °C - 166 °C. FT-IR (ν_{max}/cm^{-1}, 1630 ($C{=}N_{imine}$), 1602 ($C{=}N_{pyridyl}$). ^1H NMR: DMSO-d_6, δ (ppm): 7.96 (br s, 1H, H_{pyr}), 7.32 (m, 1H, H_{pyr}), 6.47 (m, 2H, H_{pyr}), 5.78 (d, ^3J = 12 Hz, 4H, $H_{p\text{-}cym}$), 4.76 (s, 2H, $H_{ferrocene}$), 4.54 (s, 2H, $H_{ferrocene}$), 4.22 (s, 5H, $H_{ferrocene}$), 2.80 (m, 1H, $H_{p\text{-}cym}$), 2.33 (s, 3H, H_{methyl}), 2.07 (s, 3H, $H_{p\text{-}cym}$), 1.17 (d, ^3J = 24 Hz, 6H, $H_{p\text{-}cym}$). Elemental Anal. Calc. for $C_{27}H_{30}ClFeN_2Ru$ (%): C, 53.13; H, 4.95; N, 4.95. Found: C, 53.10; H, 4.98; N, 4.93. HR-ESI-MS: *m/z* = 574.9296 for $[M]^+$, 575.9304 for $[M+H]^+$. E_{pa} = 0.58 eV, 0.38 eV; E_{pc} = 0.41 eV, E_{pc} = 0.33 eV.

2.6. *Synthesis and characterization of Ru-ferrocenyl complex 3*

L2 (0.0252 g, 0.080 mmol) was dissolved in 20 ml of methanol and transferred to a round bottomed flask. To the stirring ligand was added the ruthenium precursor $[RuCl_2(p\text{-cymene})]_2$ (0.0243 g, 0.040 mmol) dissolved in 20 ml methanol. The solution was refluxed for 3 h. After the reaction solution was filtered by gravity and solvent was removed under reduced pressure to afford an orange brown solid as product. Yield (0.032 g, 62%). Melting Point: 73 °C - 75 °C. FT-IR (ν_{max}/cm^{-1}, 1632 ($C{=}N_{imine}$), 1604 ($C{=}N_{pyridyl}$). ^1H NMR: DMSO-d_6, δ (ppm): 9.11 (s, 1H, H_{pyr}), 7.94 (s, 1H, H_{pyr}), 7.52 (t, ^3J = 15.2 Hz, 2H, H_{pyr}), 5.88 (d, ^3J = 29 Hz, 2H, $H_{p\text{-cym}}$), 5.74 (d, ^3J = 29 Hz, 2H, $H_{p\text{-cym}}$), 4.76 (s, 2H, $H_{ferrocene}$), 4.54 (s, 2H, $H_{ferrocene}$), 4.35 (s, 1H, CH_2) 4.22 (s, 5H, $H_{ferrocene}$), 4.12 (m, 1H, CH_2) 2.69 (m, 1H, $H_{p\text{-cym}}$), 2.32 (s, 3H, H_{methyl}), 2.06 (s, 3H, $H_{p\text{-cym}}$), 1.16 (m, 6H, $H_{p\text{-cym}}$). $^{13}C\{^1H\}$ NMR: DMSO-d_6, δ (ppm): 158.9, 147.6, 141.0, 131.0, 106.2, 99.8, 96.6, 88.8, 86.2, 85.2, 79.8, 78.9, 71.9, 69.3, 30.8, 29.8, 26.8, 21.5, 17.2. Elemental Anal. Calc. for $C_{32}H_{44}ClFeN_2Ru$ (%): C, 56.15; H, 6.48; N, 4.09. Found: C, 56.12; H, 6.45; N, 4.06. HR-ESI-MS: *m/z* = 685.5267 $[M+H]^+$. E_{pa} = 0.44 eV, 0.32 eV; E_{pc} = 0.43 eV, E_{pc} = 0.30 eV.

2.7. *Synthesis and characterization of Rh-ferrocenyl complex 4*

The rhodium precursor $[RhCl(COD)]_2$ (0.115 g, 0.233 mmol) was dissolved in 20 ml dichloromethane and left to stir. To this was added L2 (0.148 g, 0.465 mmol) in 20 ml dichloromethane and this was left to stir at room temperature for 16 h. The mixture was filtered by gravity and the solvent was reduced to 5 ml. Diethyl ether (20 ml) was added to the reduced solution and the mixture was filtered by gravity to obtain a bright yellow filtrate. The solvent was removed from the filtrate and solid dried under vacuum to recover the product. Yield (0.115 g, 85%). Melting Point: 150 °C - 152 °C. FT-IR (ν_{max}/cm^{-1}, 1655 ($C{=}N_{imine}$), 1604 ($C{=}N_{pyridyl}$). ^1H NMR: DMSO-d_6, δ (ppm): 6.55 (d, ^3J = 7.2 Hz, 2 H, H_{pyr}), 6.48 (d, ^3J = 8.2 Hz, 2 H, H_{pyr}), 5.58 (br s, 2 H, H_{COD}), 5.17 (br s, 2 H, H_{COD}), 4.78 (s, 2H, $H_{ferrocene}$), 4.56 (s, 2H, $H_{ferrocene}$), 4.24 (s, 5H, $H_{ferrocene}$), 3.98 (s, 2 H, CH_2), 2.41 (s, 3 H, H_{methyl}), 2.10 (m, 4 H, H_{COD}), 1.87 (m, 4 H, H_{COD}). $^{13}C\{^1H\}$ NMR: DMSO-d_6, δ (ppm): 173.1, 159.8, 148.1, 142.4, 104.2, 96.8, 85.1, 84.1, 79.4, 70.0, 69.6, 29.1, 27.9, 20.6, 17.4. Elemental Anal. Calc. for $C_{29}H_{39}ClFeN_2Rh$ (%): C, 57.12; H, 6.45; N, 4.59. Found: C, 57.11; H, 6.43; N, 4.58. HR-ESI-MS: *m/z* = 529.2314 $[M-Cl]^+$. E_{pa} = 0.42 eV, 0.30 eV; E_{pc} = 0.40 eV, E_{pc} = 0.31 eV.

2.8. *General procedure for the catalytic experiments*

Catalytic experiments were carried out in stainless steel reactors with magnetic stirrers. The products were analyzed using gas chomatography using n-decane as internal standard. In a typical run a toluene solution (5 ml) containing either Rh ferrocenyl or Ru ferrocenyl catalyst (0.00287 mmol), 1-octene (6.37 mmol) and n-decane (1.23 mmol) were transferred into the stainless steel reactor. This was pressurized to the appropriate pressure and heated at the desired temperature for 8 h. After the reaction the reaction vessel was cooled and the excess syngas vented slowly. All reactions were perfomed in duplicate and standard deviations reported.

3. Results and discussion

3.1. *Synthesis and characterization of ferrocenyl ligands L1 and L2*

L1 and L2 were synthesized by reacting acetyl ferrocene with either 2-aminopyridine or picolylamine in ethanol and dichloromethane, respectively. Catalytic amounts of formic acid were added to the reaction during the synthesis of L1. After drying the reaction mixture both ligands were afforded as deep red air stable solids in good yields (91% and 75%, respectively). Both ligands were characterized using ^{1}H NMR, ^{13}C NMR, infrared spectroscopy and high resolution ESI-mass spectrometry.

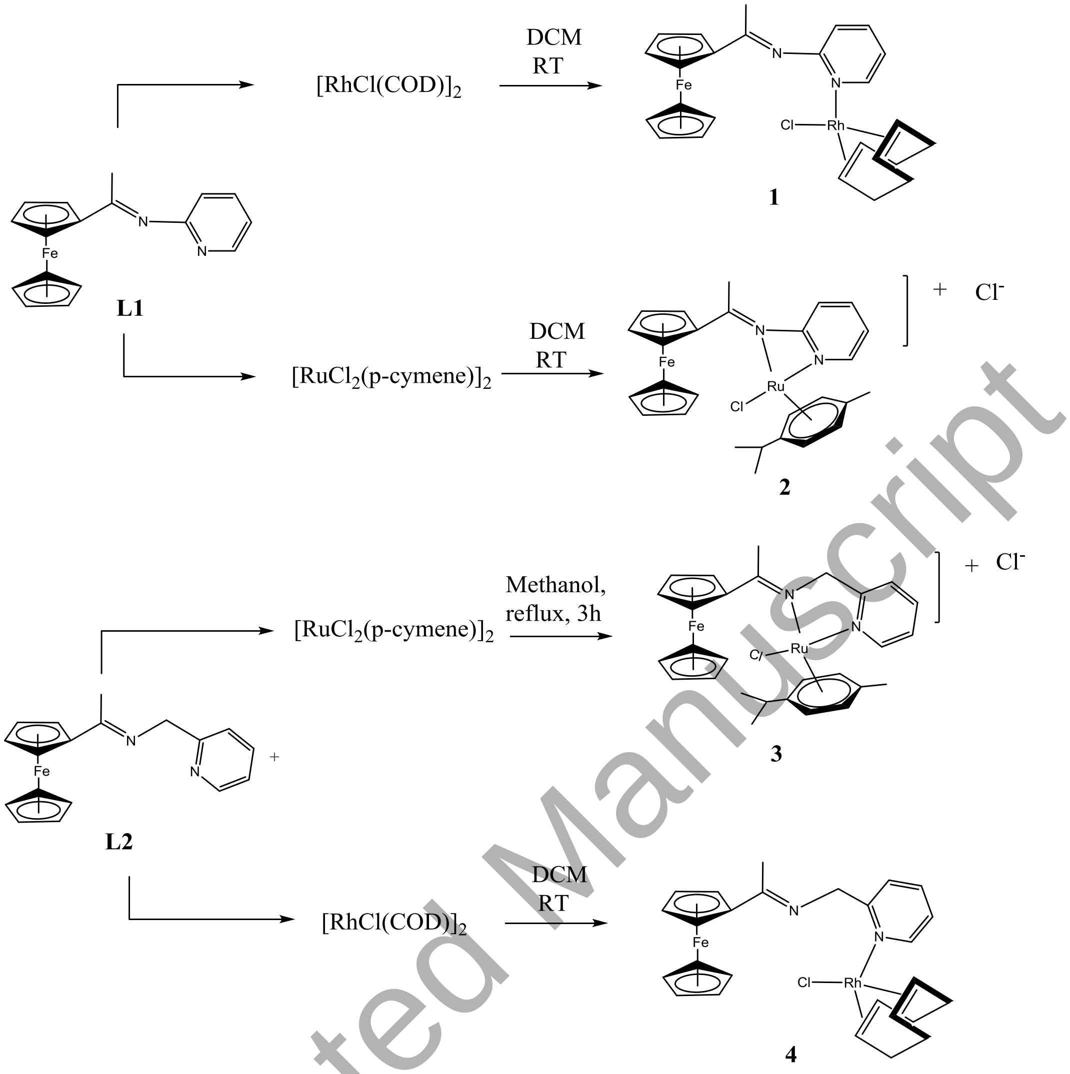
In the ^{1}H NMR spectra of both ligands, the signals for the pyridyl ring protons are observed between 6.50 ppm and 8.80 ppm. Further upfield between 4.00 ppm and 5.00 ppm the ferrocenyl protons are observed as 3 singlets, each integrating for two, two and five protons, respectively. For L2 a multiplet integrating for two protons is observed at 1.23 ppm for the CH_2 functionality. The infrared spectrum of L1 reveals the presence of a C=N functionality as an intense band at 1655 cm^{-1}. This intense band has a shoulder at 1581 cm^{-1} due to the presence of pyridyl C=N functionality. For L2, an intense absorption is observed at 1619 cm^{-1} for the C=N functional group and similar to L1 this band has a shoulder at 1594 cm^{-1} for the pyridyl C=N.

Both ligands were also characterized using high resonance ESI-MS and peaks were observed at m/z = 327.1714 for $[M+Na]^{+}$ and m/z = 319.0898 for $[M+H]^{+}$ for L1 and L2, respectively. The number of C signals observed in the ^{13}C NMR spectra of the ligands corresponds to the number for C atoms in the ligands.

3.2. ***Synthesis and characterization of ferrocenyl Rh(I) and Ru(II) complexes 1-4***

L1 and L2 were used in the synthesis of **1**-**4** using either [RuCl$_2$(p-cymene)]$_2$ [27] or [RhCl(COD)]$_2$ [28] precursors. The complexes were prepared by reacting two equivalents for each ligand to one equivalent of the dimeric precursor and allowed to stir at room temperature in dichloromethane or reflux in methanol in the case of **3** (scheme 1). The complexes recovered as red brown solids (**3**-**4**) and bright yellow (**1**-**2**) were characterized using various spectroscopic and analytical techniques. The complexes are stable in air and are soluble in dichloromethane, methanol, chloroform and DMSO.

The ^{1}H NMR spectra for **1** and **4** are very similar. The only difference is that for **4** there is a signal for the CH$_2$ protons adjacent to the pyridyl ring whereas this is absent in **1**. Upon complexion of Rh to the ferrocenyl ligand a characteristic shift of the proton adjacent to the pyridyl nitrogen from 8.45 ppm in free L1 to 7.93 ppm in **1** and 6.55 ppm in **4** is observed. This is evidence of Rh coordination to the pyridyl nitrogen. The monodentate coordination of Rh to the ligand was further confirmed using infrared spectroscopy. The infrared spectrum of L1 shows an intense C=N absorption for the imine functionality at 1655 cm^{-1}, with a shoulder at 1581 cm^{-1} for the pyridyl functionality. Upon coordination of Rh to L1 there is no shift in the band for the imine functionality while the pyridyl C=N appears at 1622 cm^{-1} (**1**) and 1604 cm^{-1} (**4**), which is indicative of Rh coordination to the pyridyl nitrogen only. This is similar to what has been previously reported in the literature for similar compounds [10, 29].



Scheme 1. Preparation of heterobimetallic **1**-**4**.

Similar to **1** and **4**, an upfield shift is observed for the proton adjacent to the pyridyl nitrogen in the Ru complexes from 8.46 ppm to 7.96 ppm (**2**) and 9.11 ppm (**3**). This is evidence of Ru coordination to the pyridyl nitrogen. The ^{1}H NMR spectrum of **2** is shown in figure 1.

The pyridyl protons are the most deshielded protons and observed between 7.00 ppm and 8.00 ppm. The aromatic p-cymene protons are observed as a doublet with a coupling constant of 12 Hz. This is further evidence of complexation of L1 to Ru. In the dimeric precursor, the aromatic protons of the p-cymene are observed as two doublets. This change in splitting pattern is evidence of coordination. The cyclopentadienyl protons of the ferrocenyl moiety are observed as singlets between 4.00 ppm and 5.00 ppm integrating for 2, 2 and 5 protons. The isopropyl and methyl protons are further upfield in the spectrum as expected.

The infrared spectrum of the complexes confirm coordination of Ru to L1 and L2. The imine functionality is observed at 1630 cm^{-1} (**2**) and 1632 cm^{-1} (**3**), which is a shift from 1655 cm^{-1} in free L1 and 1640 in L2. The pyridyl C=N functionality in the complex is observed at a higher wavenumber, indicative of bidentate Ru coordination to the ligand. The ^{1}H NMR spectrum for **3** is similar to that of **2**. The only difference is the presence of two signals between 4.00 ppm and 4.50 ppm which integrate for one proton each. These two diastereotopic protons of the CH_2 group occur in different chemical environments due to the presence of Ru. All the complexes have been characterized using ^{13}C NMR spectroscopy and the number of carbon atoms present corresponds to the signals observed in the spectra. The high resolution ESI-mass spectra of the complexes were performed in the positive-ion mode and they confirm the proposed structures. **1** shows a peak at *m/z* = 551.0173 for $[M]^+$ while **2** displays a peak at *m/z* = 575.9304 $[M+H]^+$ where M is the cation. The peaks for **3** and **4** are observed at *m/z* = 685.5267 and *m/z* = 529.2314, respectively. Several attempts were made to grow crystals suitable for single crystal X-ray diffraction, but all attempts were unsuccessful.

3.3. *Electrochemistry*

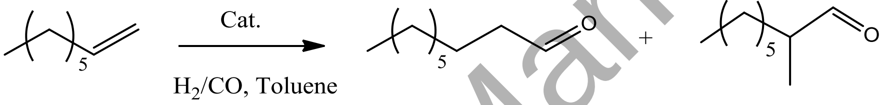
The Rh and Ru ferrocenyl complexes (**1**-**4**) and L1 and L2 were analyzed by electrochemical methods. The cyclic voltammograms were recorded in ethyl acetate at a scan rate of 20 mV/s on a glassy carbon electrode. For all analyses, ferrocene was used as the standard and the ferrocenyl ligands and complexes were analyzed in order to observe the redox processes occurring before and after either Ru or Rh is introduced to the ligand. A comparison of the wave potentials of free L1 and L2 with those of the corresponding complexes was done and results show that **1**-**4** exhibit similar voltammetric behaviors with no shifts to more positive or negative potentials upon complexation of either Rh or Ru. A representative diagram of the voltammograms is shown in figure 2.

The ferrocene standard exhibits a one electron reversible wave with $E_{1/2}$ = 0.13 V relative to the Ag/Ag^+ reference electrode. L1 and L2 show two anodic peaks; for Fe(II) to Fe(III) at 0.35 V and 0.36 V, respectively. A second peak is attributed to a one electron oxidation of the pyridine nitrogen 0.57 V for L1 and 0.58 V for L2. The oxidation of ferrocene is irreversible in both ligands with only one cathodic peak observed at 0.43 V and 0.40 V for L1 and L2, respectively, due to a one electron reduction of nitrogen on the pyridine moiety.

Upon complexation of either Ru or Rh two oxidation waves and two reduction waves are observed and are very similar in **1-4**. This means the Fe(III) to Fe(II) redox process only occurs when a second metal is present, revealing that the ferrocene moiety is less stable upon introduction of either Rh or Ru and hence reversible oxidation is observed for **1-4**.

3.4. ***Hydroformylation of 1-octene using 1-4 as catalyst precursors***

The heterobimetallic complexes **1**-**4** were tested as catalyst precursors in the hydroformylation of 1-octene in the presence of 1:1 H_2/CO (scheme 2). The reaction products were analyzed on the GC and turnover frequencies reported are based on the amount of aldehydes formed. All experiments were performed in dublicate and the average result is reported.



Scheme 2. Hydroformylation of 1-octene using **1**-**4**.

The catalytic systems comprised of toluene (solvent), internal standard (n-decane), the substrate (1-octene) and the heterobimetallic catalyst precursor. This was pressurized, heated to the desired temperature and stirred for 8 h in the presence of syngas. At the end of the experiment, the reaction vessel was cooled and the reaction mixture was analyzed using gas chomatography. The reaction pressure used was based on previous reports for Rh ferrocenyl catalyst precursors for the hydroformylation of 1-octene (40 bar, 30 bar and 20 bar) (table 1) [14, 25]. However for the less active Ru ferrocenyl catalyst precursors high pressure (40 bar and 50 bar) and temperature (100 °C and 120 °C) [10] were used as shown in table 1. The Rh ferrocenyl catalyst precursors (**1** and **4**) gave moderate to excellent results in the catalytic reactions. Both catalysts display excellent aldehyde chemoselectivity under the reaction conditions tested. **1** has the lowest turnover frequency at 40 bar and 75 °C while the best activity for both **1** and **4** is observed at 30 bar and 95 °C. The regioselectivities of the catalyst precursors vary as temperature and pressure conditions are varied.

3.4.1. Effect of pressure. The effect of pressure on the activity and regioselectivity of **1** and **4** in the hydroformylation of 1-octene was investigated at 95 °C because at this temperature both catalysts displayed good turnover frequency. The pressure was increased from 20 bar to 50 bar and the results obtained are summarized in figure 3. The results show that for both catalysts there is generally good regioselectivity for branched aldehydes with less than 40% nonanal formed. Almost 100% conversion is observed at 40 bar and 30 bar, however at 20 bar less than 80% 1-octene conversion is observed with **4**. Decreasing the pressure also resulted in slight drop in the amount of branched aldehydes formed with **4**. Lowering the pressure did not have a significant effect on the performance of **4**. It has been previously reported that the pressure of syngas has an influence on the n:iso ratios obtained during hydroformylation hence the varying regioselectivity under different conditions [30].

3.4.2. Effect of temperature. The influence of temperature was also investigated at 30 bar for both **1** and **4**. The temperature was varied from 75 °C to 95 °C for both catalysts. The results are summarized in figure 4. The conversion of 1-octene to aldehydes increased to >99% when the temperature was increased from 75 °C to 95 °C. The product distribution for both **1** and **4** also changed significantly showing that low temperature suppresses the hydroformylation reaction. The conversion of 1-octene to aldehydes increased to >99% when the temperature was increased from 75 °C to 95 °C. The product distribution for both **1** and **4** also changed significantly showing that low temperature suppresses the hydroformylation reaction. Catalyst precursor **1** displays good catalytic activity at 95 °C (275 h^{-1}) with good regioselectivity (64%) for branched aldehydes. However, when the temperature is lowered to 75 °C, the regioselectivity of the catalyst changes to give 78% nonanal. Figure 3 shows that at 95 °C catalyst **4** performs best with poor results being recorded at 75 °C. The good catalytic perfomance for **1** and **4** observed at high temperature could be due to the faster generation of the catalytically active species. Caiazzo and co-workers have reported that the regioselectivity towards branched aldehydes increases at elevated temperatures [31]. This could be due to the preferential formation of the branched alkyl intermediate during the catalytic cycle at higher reaction temperatures as a result of higher rates of 1-octene isomerization. Catalysts **1** and **4** show comparable activity and the presence of the CH_2 moiety in **4** did not result in varying chemoselectivity as both catalysts show 100%

chemoselectivity towards aldehydes. These catalysts are slightly less active than the Rh ferrocenyl complexes previously (>300 h^{-1}) reported in the hydroformylation of 1-octene [25] but show similar chemoselectivity towards aldehydes. Some high pressure NMR experiments were conducted in order to elucidate whether the mechanism proceeds *via* a Rh-H species which could be the active species. Unfortunately, no hydride peaks were observed.

The hydroformylation reaction was also performed using the Ru ferrocenyl (**2** and **3**) catalyst precursors, but they did not give any conversion of 1-octene or activity under the same conditions the Rh precatalysts were tested (20 bar - 40 bar; 75 °C – 95 °C). This shows that **2** and **3** are less active than their Rh counterparts. Higher temperatures and pressures were used for hydroformylation using the Ru derivatives and therefore a direct comparison of the precatalysts cannot be made because they were tested under different conditions. The results are summarized in table 2.

2 and **3** were tested at 40 bar and 50 bar while the temperature was varied from 100 °C and 120 °C; **2** gave 68% 1-octene conversion at 100 °C and 40 bar and these conditions gave the best results for this catalyst. The activity was 186 h^{-1} with 57% of the aldehydes formed being nonanal. When the pressure and temperature were raised further, poor conversions were recorded.

For Ru ferrocenyl catalyst **2** the best conversion was obtained at 100 °C and 50 bar pressure with an activity of 148 h^{-1}. However, the catalyst formed a 1:1 mixture of linear to branched aldehydes. When the temperature was raised to 120 °C, the catalytic activity dropped drastically probably due to catalyst degradation under the high pressure. At 100 °C, **2** displays excellent nonanal regioselectivity with no formation of branched aldehydes observed at both 40 bar and 50 bar. However, the % conversion of 1-octene is low, showing improvement when both temperature and pressure are raised. At 120 °C and 40 bar **3** does not show any 1-octene conversion to products and even when the pressure is raised to 50 bar, only 10% conversion is observed. This shows that **3** requires very high temperatures (>120 °C) and pressure (>50 bar) and longer reaction times in order for effective 1-octene conversions to be observed as previously observed [10, 18, 32]. No hydrogenation products (octane or nonanol) were observed with the Ru ferrocenyls precatalysts as expected for Ru catalysts [10].

Catalytic reactions were performed in the presence of mercury in order to determine whether the catalytic system was entirely homogeneous. No significant changes were observed in the conversions and activity of the systems in the presence of mercury which confirmed the homogeneity of the catlytic system.

4. Conclusion

Two new ferrocenyl ligands, L1 and L2, were synthesized and characterized using various spectroscopic and analytical techniques. Both ligands were used to prepare new Rh(I) and Ru(II) ferrocenyl complexes **1**-**4**. The Rh complex **1** coordinated to L1 in a monodentate fashion while Ru coordinated bidentate to L1 for the cationic complexes **2** and **3**. The structures of all the complexes were confirmed using ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy, high resolution electrospray ionization mass spectrometry, infrared spectroscopy and elemental analysis. **1-4** have been tested as catalyst precursors in the hydroformylation of 1-octene with all displaying excellent aldehyde chemoselectivity. The rhodium ferrocenyl complexes (**1** and **4**) generally have better activity than **2** and **3**. At high temperatures the Rh ferrocenyl catalyst precursors showed better regioselectivity for branched aldehydes as a result of increased isomerization of 1-octene at elevated temperatures, which were consequently converted to the branched aldehydes. The mercury drop experiment confirmed that all the catalytic systems are homogeneous.

Acknowledgements

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Conflict of interest

There are no conflicts to declare.

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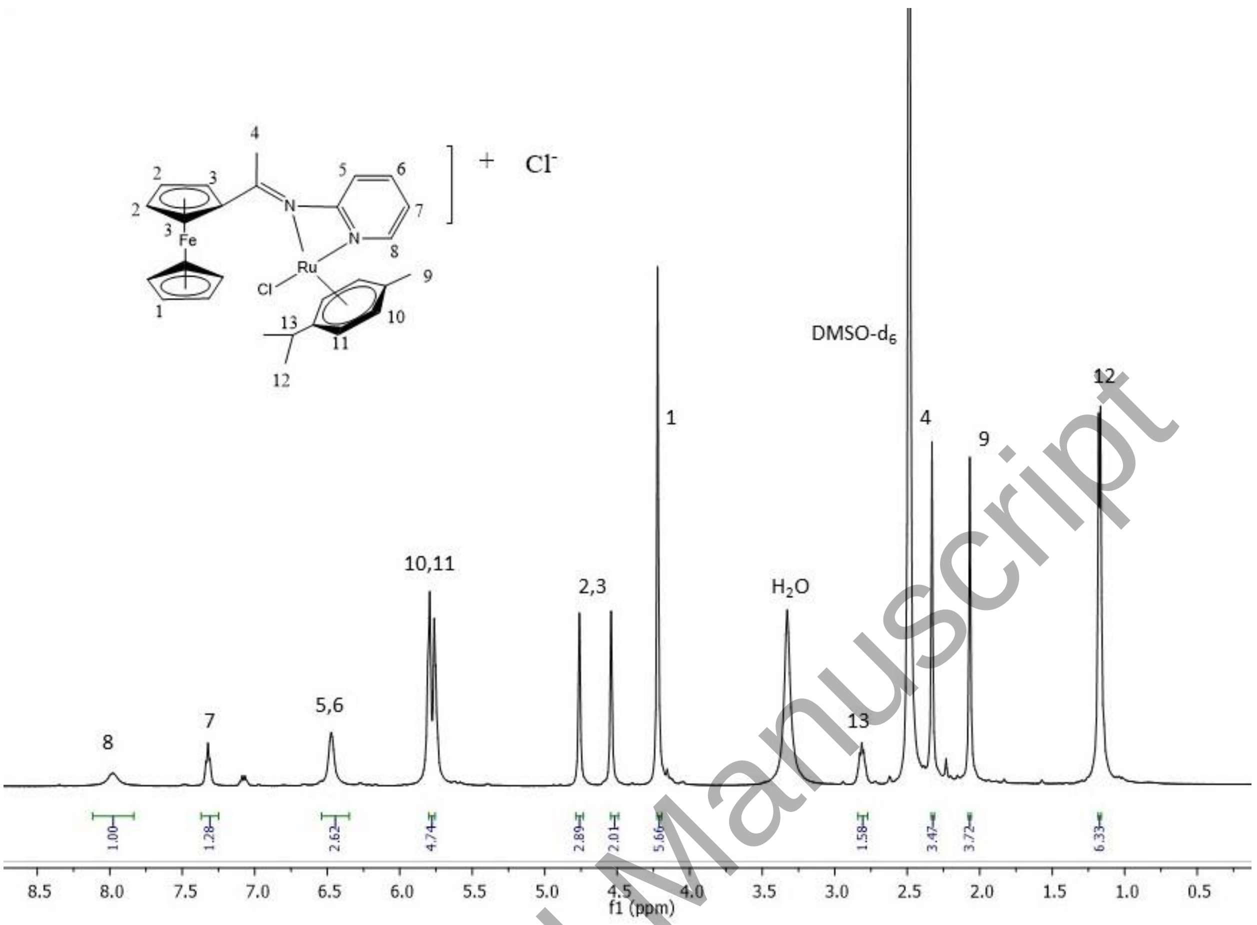

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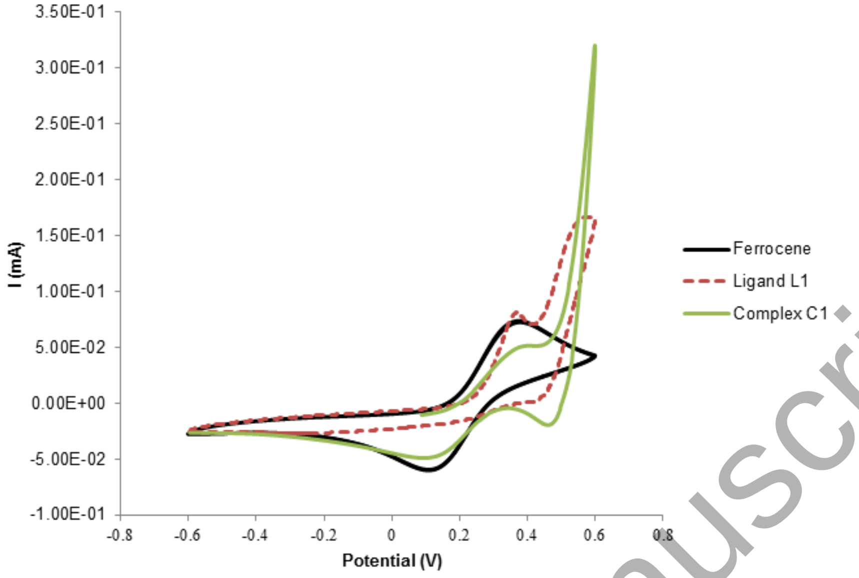
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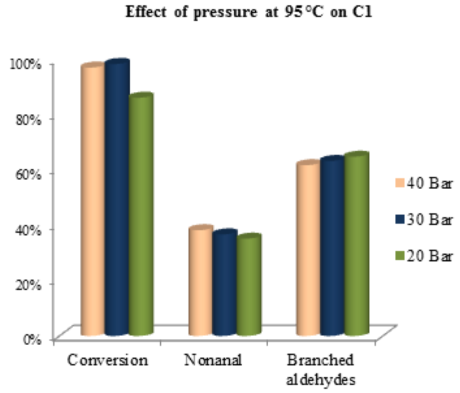
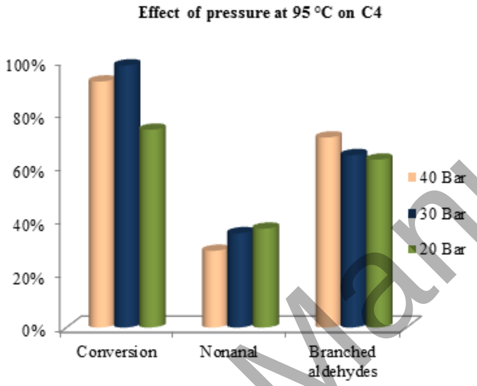
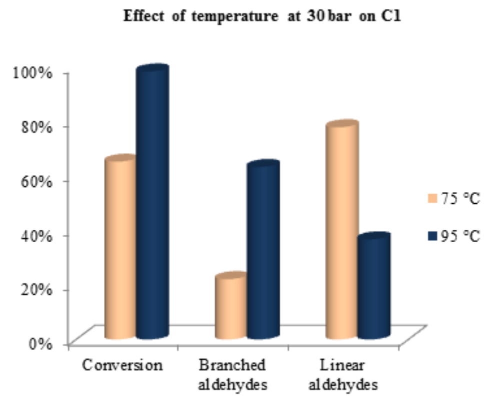
Ferrocene
Ligand L1
Complex C1


Effect of pressure at 95 °C on C1


Effect of pressure at 95 °C on C4


Effect of temperature at 30 bar on C1

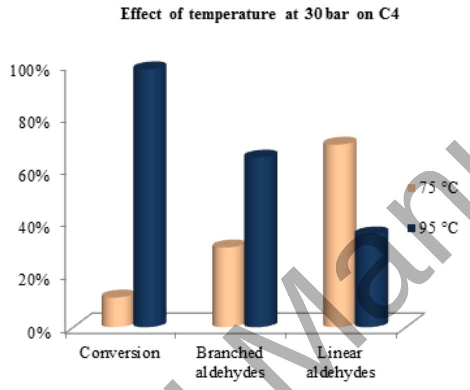
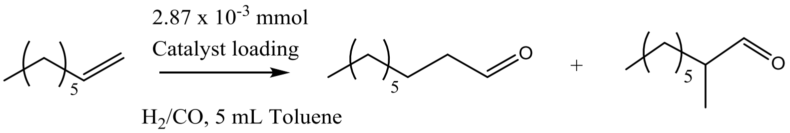

Effect of temperature at 30 bar on C4

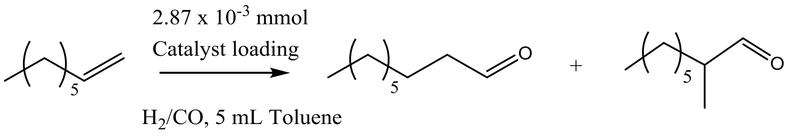
Table 1. Hydroformylation of 1-octene using Rh ferrocenyl catalyst precursors **1** and **4**.



Pressure	Temperature	Catalyst	Conversion %	TOF	Aldehydes	Linear aldehydes	Branched aldehydes (%)	n/iso
20 Bar	75 °C	**1**	65.22	180	100	77	23	3.50
	95 °C	**1**	86.13	238	100	35	65	0.54
30 Bar	75 °C	**1**	78.15	215	100	51	49	1.02
	95 °C	**1**	98.33	272	100	37	63	0.58
40 Bar	75 °C	**1**	93.50	248	100	67	33	1.99
	95 °C	**1**	97.05	268	100	38	62	0.62
20 Bar	75 °C	**4**	75.39	208	100	46	54	1.19
	95 °C	**4**	74.16	205	100	37	63	0.58
30 Bar	75 °C	**4**	91.31	231	100	70	30	2.28
	95 °C	**C4**	98.28	271	100	35	65	0.54
40 Bar	75 °C	**C4**	64.43	178	100	70	30	2.28
	95 °C	**C4**	92.23	255	100	23	77	0.40

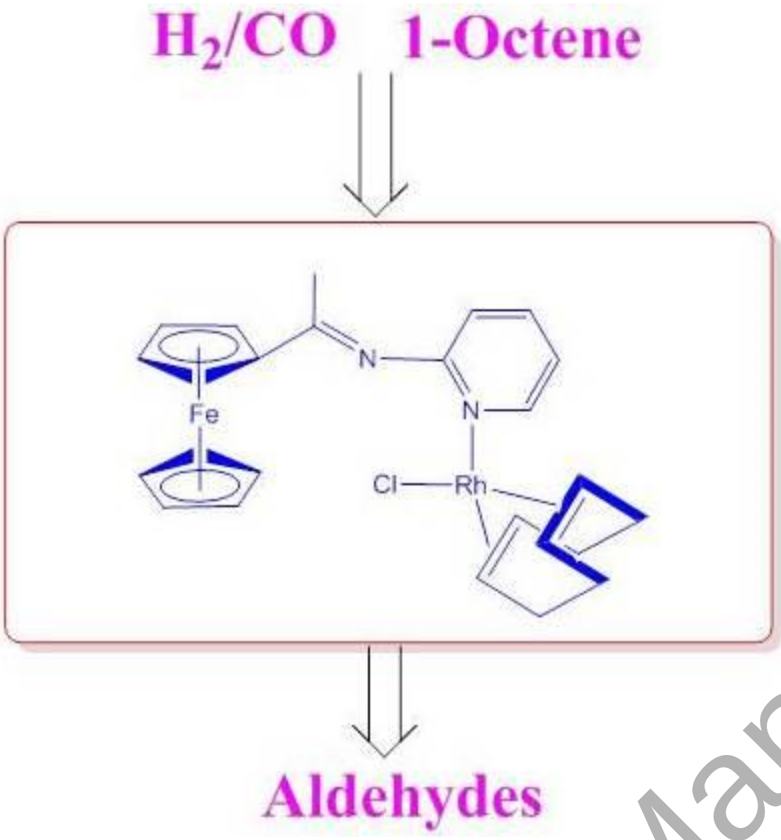
The reactions were performed in a 30 mL stainless steel pipe reactor. The reactor was charged with toluene (5 mL), 1-octene (6.37 mmol), internal standard *n*-decane (1.26 mmol) and Rh loading (2.87×10^{-3} mmol), 8 h. The reactor was flushed with nitrogen thee times, followed by flushing twice with syngas (1:1, CO: H2). TOF = (mmol of aldehydes/mmol of Rh)/8 h. Standard deviation of conversions: ±0.29, ±0.78, ±1.12, ±0.19, ±0.45, ±1.02. ±0.98, ±0.44, ±0.31, ±0.29, ±0.78, ±1.05.

Table 2. Hydroformylation of 1-octene using Ru ferrocenyl catalyst precursors **2** and **3**.



Pressure	Temperature	Catalyst	Conversion %	TOF	Aldehydes	Linear aldehydes	Branched aldehydes (%)	n/iso
40 Bar	100 °C	**2**	27	74	100	100	-	-
	120 °C	**2**	16	451	100	38	62	0.62
50 Bar	100 °C	**2**	15	40	100	100	-	-
	120 °C	**2**	56	156	100	61	39	1.54
40 Bar	100 °C	**3**	68	186	100	57	43	1.33
	120 °C	**3**	-	-	-	-	-	-
50 Bar	100 °C	**3**	98	148	100	49	51	0.98
	120 °C	**3**	10	161	100	84	16	5.08

The reactions were performed in a 30 mL stainless steel pipe reactor. The reactor was charged with toluene (5 mL), 1-octene (6.37 mmol), internal standard *n*-decane (1.26 mmol) and Ru loading (2.87×10^{-3} mmol). The reactor was flushed with nitrogen thee times, followed by flushing twice with syngas (1:1, CO: H2). TOF = (mmol of aldehydes/mmol of Ru)/time. Standard deviations of conversions: ±0.30, ±0.38, ±0.12, ±1.09, ±0.75, ±1.32. ±1.18, ±0.54.


H2/CO
1-Octene
Fe
N
N
Cl
Rh
Aldehydes