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FULL PAPER

Rhodium-catalysed hydroformylation of 1-octene using aryl and ferrocenyl Schiff base-derived ligands

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Monometallic and heterobimetallic complexes of Rh(I) bearing chelating *N*,*O*-bidentate aryl- and ferrocenyl-derived ligands have been synthesised via Schiff base condensation reactions, and characterised fully using ^{1}H NMR, ^{13}C{^{1}H} NMR and Fourier transform infrared spectroscopies, elemental analysis and mass spectrometry. The new monometallic and heterobimetallic complexes were evaluated as potential catalyst precursors in the hydroformylation of 1-octene at 95°C and 40 bar. The ferrocenylimine mononuclear compounds were inactive in the hydroformylation experiments. The Rh(I) monometallic and the ferrocene–Rh(I) heterobimetallic pre-catalysts displayed good activity and conversion of 1-octene as well as outstanding chemoselectivity towards aldehydes in the hydroformylation reaction.

KEYWORDS

Ferrocene, homogeneous catalysis, hydroformylation, rhodium, Schiff base

1 | INTRODUCTION

Hydroformylation is one of the important transition metal complex-catalysed reactions in industry, producing approximately 10 million tonnes of aldehydes per annum.[1–4] This atom-economical reaction involves the addition of carbon monoxide and hydrogen across a double bond to form aldehydes as major products, and occasionally isomerisation products which are equally important for downstream processes/applications.

The hydroformylation reaction has been used successfully in the Rührchemie/Rhône-Poulenc process for the production of C4 and C5 aldehydes from propene and butene, respectively.[5–7] The principal metal used in the design of catalysts for hydroformylation is rhodium because of its remarkable catalytic activity under mild reaction conditions.[8–11] Rhodium complexes bearing hemilabile ligands have been reported extensively in the literature.[12–14] Among these ligands are the Schiff base ligands, which result from a condensation reaction between an amine and an aldehyde or ketone, producing imines.[15–21] These ligands are very popular because of their good stability and versatility in organometallic chemistry.[22–24]

In the past, we have reported on the synthesis and catalytic evaluation of Rh(I) complexes bearing Schiff base ligands containing *N*,*O*-chelates.[25–27] These catalyst precursors have exhibited good to excellent catalytic activity in the hydroformylation of 1-octene. However, the chemo- and regioselectivity properties of the monomeric complexes have been moderate. This has led to the need for the design of catalyst precursors that can possibly be exclusive to aldehydes only, and that can show a bias towards either branched or linear aldehydes.[28] Reduction of the amount of side-products (for example, isomers) is in-line with green chemistry principles.[29,30] Recent reports also indicate that an approach to obtaining good catalytic activity and selectivity has been through incorporation of a second metal, resulting in either homobimetallic or heterobimetallic systems.[31–37]

Having two different metals can offer more diverse applications of a catalyst, where both metals can perform different tasks that may lead to improved catalytic activity and selectivity towards the intended product.[38–40] Such an approach emanates from naturally occurring metalloenzymes which often possess two or more different metals, and as a result exhibit improved catalytic properties.[41–43] Ferrocene has proven to be a candidate of interest owing to the presence of ligation sites on its cyclopentadienyl rings, allowing for the ease of modification of ferrocene as a building block for organometallic complexes.[44] Moreover, the incorporation of ferrocene stems from its redox activity, versatility and thermal and chemical stability that can be critical when ferrocene

is used as a platform of support in functional or ancillary ligands.[45,46] Several ferrocenylaryl–Rh(I) heterobimetallic pre-catalysts have been reported in the hydroformylation of olefins, with phosphorus donor sites having been predominantly used to provide the required modification of the ferrocene moiety.[47–54]

Herein, we report the synthesis and characterisation of new Rh(I) aryl- and ferrocenyl-derived complexes and their catalytic evaluation in the hydroformylation of 1-octene.

2 | EXPERIMENTAL

2.1 | Materials and methods

All reactions were carried out in air unless otherwise stated. All chemicals and solvents were of reagent grade and used as received from Sigma-Aldrich, unless otherwise stated. $RhCl_3{\cdot}3H_2O$ was purchased from Heraeus South Africa (Pty) Ltd. The *N*-phenylsalicylaldimine ligands **1a** and **1b** were synthesised according to previously reported procedures.[26] NMR spectra were recorded with either a Bruker Biospin (^{1}H: 400.22 MHz; ^{13}C: 100.65 MHz) or a Varian XR300 (^{1}H: 300.08 MHz; ^{13}C: 75.46 MHz) spectrometer (see supporting information for assignments). NMR values are reported relative to the internal standard tetramethylsilane (0.00 ppm). Fourier transform infrared (FT-IR) spectra were recorded using attenuated total reflectance mode. Melting points were determined using a BÜCHI B-540 melting point apparatus. Mass spectrometry was carried out using a JEOL GC Mate II single magnetic mass spectrometer in the positive-ion mode. Elemental analyses were carried out using a Fission EA 110 CHNS analyser. Analyses and quantification of the catalytic products was carried out using a PerkinElmer Clarus 580 GC instrument equipped with a flame ionisation detector and 30 m capillary column. Single-crystal X-ray data collections for **2a** and **5a** were carried out with a Nonius Kappa CCD diffractometer at 173(2) K using an Oxford Cryostream-600. Data reduction and cell refinement were performed using DENZO,[55] and the space group was determined from the systematic absences by XPREP.[56] Structure solution and refinement were performed using the crystallographic suite OLEX2 which was also used to generate the molecular diagrams.[57] The structures were solved by direct methods, implemented in SHELXT-97,[58] and the subsequent refinement proceeded using the full-matrix least-squares method, based on F^2 values against all reflections, including anisotropic displacement parameters for all non-hydrogen atoms, as implemented in SHELXL-2014/7.[58] Despite using SADABS to apply absorption correction to the data of compound **2a**,[56] several high-intensity residual peaks remained which did not correspond to non-modelled atoms or disorder. CCDC reference numbers 1441988 and 1441989 for compounds **2a** and **5a**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.2 | Preparation of Rh(I) mononuclear complex 2a

A solution of triethylamine (5.10×10^{-2} g, 0.499 mmol) in ethanol (5 cm^3) was added to a stirring solution of ligand **1a** (9.83×10^{-2} g, 0.498 mmol) in ethanol (10 cm^3) and the solution was left stirring at room temperature for 30 min. $[RhCl(COD)]_2$ (COD =1,5-cyclooctadiene) (0.123 g, 0.249 mmol) in ethanol (10 cm^3) was added dropwise and the mixture was stirred at room temperature overnight. The solvent was reduced to *ca* 10 cm^3 and a dichloromethane–water wash was carried out in a 100 cm^3 separating funnel to remove excess triethylamine. The dichloromethane solution was collected, dried over anhydrous magnesium sulfate, filtered and the solvent was removed under reduced pressure, to yield a yellow solid product which was collected and dried *in vacuo*.

Yield 0.164 g (81%); m.p. 248.3–248.9°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.98 (s, 1H, H^7), 7.38–7.32 (m, 3H, H$^{9;5}$), 7.24–7.14 (m, 2H, H$^{4;3}$), 7.06–7.03 (m, 2H, H^{10}), 6.91 (d, ^3J = 9.0 Hz, 1H, H^2), 6.58 (m, 1H, H^{11}), 4.70–4.52 (m, 2H, H^{12}), 3.29–3.11 (m, 2H, H$^{12'}$), 2.52–2.22 (m, 4H, H^{13}), 1.92–1.69 (m, 4H, H$^{13'}$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm): 166.9 (C^1), 165.6 (C^7), 152.4 (C^8), 135.5 (C^4), 135.2 (C^5), 128.6 (C^9), 126.0 (C^3), 123.3 (C^{10}), 122.1 (C^2), 118.7 (C^6), 114.7 (C^{11}), 84.74 (C^{12}), 73.03 (C$^{12'}$), 31.38 (C^{13}), 29.01 (C$^{13'}$). FT-IR (ν_{max}, cm^{-1}): 1603 (C=N). Anal. Calcd for $C_{21}H_{22}NORh$ (%): C, 61.92; H, 5.44; N, 3.44. Found (%): C, 61.64; H, 5.66; N, 3.02. EI-MS (*m/z*) = 407.04 [M]$^+$.

2.3 | Preparation of Rh(I) mononuclear complex 2b

A solution of triethylamine (0.112 g, 1.10 mmol) in dichloromethane (5 cm^3) was added to a stirring solution of *N*-phenyl-3-*t*-butylsalicylaldimine ligand (**1b**) (0.279 g, 1.10 mmol) in dichloromethane (15 cm^3) and the solution was left stirring at room temperature for 30 min. $[RhCl(COD)]_2$ (0.272 g, 0.551 mmol) was then added and the mixture was left stirring overnight at room temperature. The solvent was reduced to *ca* 10 cm^3 and the product was extracted through a dichloromethane–water wash in a 100 cm^3 separating funnel. The dichloromethane solution was collected and the solvent was removed under reduced pressure, to yield a yellow solid product which was collected and dried *in vacuo*.

Yield 0.408 g (80%); m.p. 230.7–232.1°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.03 (s, 1H, H^9), 7.41–7.32 (m, 3H, H$^{11;7}$), 7.25–7.18 (m, 1H, H^6), 7.09–7.03 (m, 3H, H$^{12;5}$), 6.58–6.50 (m, 1H, H^{13}), 4.92–4.81 (m, 2H, H^{14}), 3.31–3.32 (m, 1H, H$^{14'}$), 2.54–2.30 (m, 4H, H^{15}), 1.96–1.71 (m, 4H, CH$^{15'}$), 1.41 (s, 1H, H^4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm): 166.2 (C^9), 165.8 (C^1), 152.6 (C^{10}), 140.5 (C^3), 134.3 (C^5), 131.8 (C^7), 128.6 (C^{11}), 125.9 (C^6), 123.5 (C^{12}), 118.8

(C^8), 114.2 (C^{13}), 83.58 (C^{14}), 72.82 ($C^{14'}$), 35.11 (C^2), 31.26 (C^{15}), 29.85 (C^4), 29.37 ($C^{15'}$). FT-IR (ν_{max}, cm^{-1}): 1595 (C=N). Anal. Calcd for $C_{25}H_{30}NORh$ (%): C, 64.79; H, 6.53; N, 3.02. Found (%): C, 64.35; H, 6.80; N, 2.56. EI-MS (m/z) = 463.14 $[M]^+$.

2.4 | Preparation of 2-Hydroxysalicylaldimine ligand 3a

A solution of hydrazine hydrate (0.381 g, 11.9 mmol) in ethanol (5 cm^3) was added to a stirring solution of salicylaldehyde (0.363 g, 2.97 mmol) in ethanol (10 cm^3) to give a light yellow solution which was refluxed for 3 h. The solvent was then reduced to a minimal amount (*ca* 5 cm^3) and excess hydrazine hydrate was removed by co-evaporation under reduced pressure with toluene (20 cm^3). The product was obtained as yellow crystals, which were washed with petroleum ether (20 cm^3) and dried *in vacuo*.

Yield 0.302 g (75%); m.p. 95.4–96.1°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 11.05 (s, 1H, H^1), 7.87 (s, 1H, H^8), 7.26–7.17 (m, 1H, H^5), 7.13–7.08 (dd, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 1H, H^3), 6.98–6.93 (d, ^3J = 8.3 Hz, 1H, H^6), 6.90–6.84 (td, ^3J = 7.5 Hz, ^4J = 1.1 Hz, 1H, H^4), 5.45 (s, 2H, H^9). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm): 157.7 (C^2), 146.8 (C^8), 130.0 (C^5), 129.3 (C^3), 119.1 (C^4), 118.5 (C^7), 116.5 (C^6). FT-IR (ν_{max}, cm^{-1}): 3380 (N−H), 3288 (N−H), 2927 (O−H), 1568 (C=N). Anal. Calcd for $C_7H_8N_2O$ (%): C, 61.75; H, 5.92; N, 20.58. Found (%): C, 61.79; H, 5.49; N, 21.03. EI-MS (m/z) = 136.05 $[M]^+$.

2.5 | Preparation of 3-*t*-Butylsalicylaldimine ligand 3b

A solution of hydrazine hydrate (2.38 g, 74.3 mmol) in ethanol (5 cm^3) was added to a stirring solution of 3-*t*-butyl-2-hydroxybenzaldehyde (3.31 g, 18.6 mmol) in ethanol (15 cm^3) and the solution was refluxed for 5 h. The solvent was then reduced to a minimal amount (*ca* 5 cm^3) and excess hydrazine hydrate was removed by co-evaporation under reduced pressure with toluene (20 cm^3). The product was obtained as yellow crystals, which were washed with petroleum ether (20 cm^3) and dried *in vacuo*.

Yield 1.91 g (53%); m.p. 79.5–80.6°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 11.61 (s, 1H, H^1), 7.91 (s, 1H, H^{10}), 7.31–7.24 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H, H^6), 7.02–6.97 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H, H^8), 6.87–6.80 (t, ^3J = 7.5 Hz, 1H, H^7), 5.38 (s, 2H, H^{11}), 1.47 (s, 9H, H^5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm): 156.9 (C^2), 147.9 (C^{10}), 137.0 (C^4), 127.8 (C^8), 127.5 (C^6), 118.5 (C^9), 118.4 (C^7), 34.86 (C^3), 29.41 (C^5). FT-IR (ν_{max}, cm^{-1}): 3398 (N−H), 3284 (N−H), 2954 (O−H), 1608 (C=N). Anal. Calcd for $C_{11}H_{16}N_2O$ (%): C, 68.72; H, 8.39; N, 14.57. Found (%): C, 68.98; H, 8.58; N, 14.83. EI-MS (m/z) = 192.10 $[M]^+$, 92%.

2.6 | Preparation of Salicylaldimineferrocenylimine mononuclear complex 4a

Ferrocenecarboxaldehyde (0.212 g, 0.992 mmol) was added to a stirring solution of ligand **3a** (0.135 g, 0.992 mmol) in ethanol (20 cm^3) and the red solution was left stirring at room temperature for 24 h. The solvent was then removed to yield a dark red crystalline product which was collected and dried *in vacuo*.

Yield 0.259 g (79%); m.p. decomposes without melting, onset occurs at 128°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 11.84 (s, 1H, H^1), 8.68 (s, 1H, H^9), 8.55 (s, 1H, H^8), 7.44–7.29 (m, 2H, $H^{5;3}$), 7.08–6.89 (m, 2H, $H^{6;4}$), 4.82–4.66 (br s, 2H, H^{11}), 4.58–4.44 (br s, 2H, H^{12}), 4.26 (s, 5H, H^{13}). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm): 163.8 (C^8), 162.6 (C^9), 159.6 (C^2), 132.4 (C^5), 132.1 (C^3), 119.4 (C^4), 118.0 (C^7), 116.9 (C^6), 71.57 (C^{12}), 69.52 (C^{13}), 69.36 (C^{10}), 69.06 (C^{11}). FT-IR (ν_{max}, cm^{-1}): 2963 (O−H), 1614 (C=N), 1586 (C=N). Anal. Calcd for $C_{18}H_{16}FeN_2O$ (%): C, 65.08; H, 4.86; N, 8.43. Found (%): C, 64.55; H, 4.52; N, 8.03. EI-MS (m/z) = 331.98 $[M]^+$.

2.7 | Preparation of 3-*t*-Butylsalicylaldimineferrocenylimine mononuclear complex 4b

Ferrocenecarboxaldehyde (0.133 g, 0.623 mmol) was added to a stirring solution of ligand **3b** (0.120 g, 0.623 mmol) in ethanol (20 cm^3) and the red solution was left stirring at room temperature for 24 h. The solvent was then removed to afford a red solid product which was collected and dried *in vacuo*.

Yield 0.214 g (89%); m.p. decomposes without melting, onset occurs at 155°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 12.45 (s, 1H, H^1), 8.69 (s, 1H, H^{11}), 8.58 (s, 1H, H^{10}), 7.42–7.35 (dd, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1H, H^8), 7.24–7.17 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H, H^6), 6.92–6.84 (t, ^3J = 7.7 Hz, 1H, H^7), 4.77–4.72 (br s, 2H, H^{13}), 4.55–4.49 (br s, 2H, H^{14}), 4.26 (s, 5H, H^{15}), 1.49 (s, 9H, H^5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm): 163.5 (C^{10}), 163.4 (C^{11}), 158.9 (C^2), 137.4 (C^4), 130.5 (C^6), 129.7 (C^8), 118.8 (C^7), 118.0 (C^9), 71.49 (C^{14}), 69.65 (C^{15}), 69.64 (C^{12}), 69.00 (C^{13}), 34.91 (C^3), 29.42 (C^5). FT-IR (ν_{max}, cm^{-1}): 2958 (O−H), 1614 (C=N), 1590 (C=N). Anal. Calcd for $C_{22}H_{24}FeN_2O$ (%): C, 68.05; H, 6.23; N, 7.21. Found (%): C, 67.66; H, 6.29; N, 6.88. EI-MS (m/z) = 388.09 $[M]^+$.

2.8 | Preparation of Salicylaldimineferrocenylimine Rh (I) 1,5-Cyclooctadiene Heterobimetallic complex 5a

A solution of triethylamine (5.63×10^{-2} g, 0.556 mmol) in dichloromethane (5 cm^3) was added to a stirring solution of **4a** (0.184 g, 0.555 mmol) in dichloromethane (15 cm^3) and the solution was left stirring at room temperature for 30 min. $[RhCl(COD)]_2$ (0.137 g, 0.278 mmol) was then added and the mixture was left stirring overnight at room temperature. The solvent was reduced to *ca* 10 cm^3 and the

product was extracted through a dichloromethane–water wash in a 100 cm^3 separating funnel. The dichloromethane solution was collected and the solvent was removed under reduced pressure, to yield a brown solid product which was collected and dried *in vacuo*.

Yield 0.296 g (98%); m.p. decomposes without melting, onset occurs at 181°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.85 (s, 1H, H^8), 7.65 (s, 1H, H^7), 7.34–7.28 (m, 1H, H^4), 7.18–7.13 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, H^2), 6.93–6.88 (d, ^3J = 8.6 Hz, 1H, H^5), 6.61–6.55 (m, 1H, H^3), 4.67–4.64 (t, ^3J = 1.8 Hz, 2H, H^{10}), 4.64–4.58 (m, 2H, H^{13}), 4.50–4.47 (t, ^3J = 1.8 Hz, 2H, H^{11}), 4.27 (s, 5H, H^{12}), 4.01–3.95 (m, 2H, $H^{13'}$), 2.58–2.41 (m, 4H, H^{14}), 2.02–1.88 (m, 4H, $H^{14'}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 166.4 (C^1), 157.7 (C^8), 152.9 (C^7), 134.2 (C^4), 134.1 (C^2), 121.8 (C^5), 117.3 (C^6), 114.6 (C^3), 85.09 (C^{13}), 73.24 ($C^{13'}$), 71.23 (C^{11}), 69.48 (C^{12}), 69.35 (C^9), 68.64 (C^{10}), 31.53 (C^{14}), 29.19 ($C^{14'}$). FT-IR (ν_{max}, cm^{-1}): 1599 (C=N), 1570 (C=N). Anal. Calcd for $C_{26}H_{27}FeN_2ORh$ (%): C, 57.59; H, 5.02; N, 5.17. Found (%): C, 57.86; H, 5.07; N, 4.70. EI-MS (*m/z*) = 332.05 $[M - Rh(COD) + H]^+$.

2.9 | Preparation of 3-*t*-Butylsalicylaldimineferrocenylimine Rh(I) 1,5-Cyclooctadiene Heterobimetallic complex 5b

A solution of triethylamine (2.49×10^{-2} g, 0.246 mmol) in dichloromethane (5 cm^3) was added to a stirring solution of **4b** (9.52×10^{-2} g, 0.245 mmol) in dichloromethane (15 cm^3) and the solution was left stirring for 30 min. $[RhCl(COD)]_2$ (6.05×10^{-2} g, 0.123 mmol) was then added and the mixture was left stirring overnight at room temperature. The solvent was reduced to *ca* 10 cm^3 and the product was extracted through a dichloromethane–water wash in a 100 cm^3 separating funnel. The dichloromethane solution was collected and the solvent was removed under reduced pressure, to afford a brown solid product which was collected and dried *in vacuo*.

Yield 0.107 g (73%); m.p. decomposes without melting, onset occurs at 198°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.87 (s, 1H, H^{10}), 7.68 (s, 1H, H^9), 7.37–7.32 (dd, ^3J = 7.4 Hz, ^4J = 1.7 Hz, 1H, H^7), 7.08–7.02 (dd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, H^5), 6.58–6.49 (t, ^3J = 7.7 Hz, 1H, H^6), 4.87–4.82 (m, 2H, H^{15}), 4.66–4.63 (t, ^3J = 1.9 Hz, 2H, H^{12}), 4.49–4.46 (t, ^3J = 1.9 Hz, 2H, H^{13}), 4.27 (s, 5H, H^{14}), 4.04–3.97 (m, 2H, $H^{15'}$), 2.58–2.45 (m, 4H, H^{16}), 2.02–1.91 (m, 4H, $H^{16'}$), 1.40 (s, 9H, H^4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 165.3 (C^1), 157.7 (C^{10}), 153.6 (C^9), 140.3 (C^3), 132.9 (C^5), 130.7 (C^7), 117.5 (C^8), 114.0 (C^6), 83.99 (C^{15}), 73.18 ($C^{15'}$), 71.13 (C^{13}), 69.97 (C^{11}), 69.65 (C^{14}), 68.60 (C^{12}), 35.13 (C^2), 31.44 (C^{16}), 29.79 (C^4), 28.81 ($C^{16'}$). FT-IR (ν_{max}, cm^{-1}): 1595 (C=N), 1577 (C=N). Anal. Calcd for $C_{30}H_{35}FeN_2ORh$ (%): C, 60.22; H, 5.90; N, 4.68. Found (%): C, 60.41; H, 5.85; N, 4.36. EI-MS (*m/z*) = 598.08 $[M]^+$.

2.10 | General procedure for catalytic experiments

In a typical experiment, the catalyst precursor (**2**, **4** and **5**) (2.87×10^{-3} mmol) was weighed 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 airtight reactor was then de-aerated by flushing three times with nitrogen gas, then charged with syngas ($CO–H_2$, 1:1 ratio) and heated to 95°C at a syngas pressure of 40 bar. At 8 h, the reactor was depressurised and the products were transferred into a vial for analysis using GC.

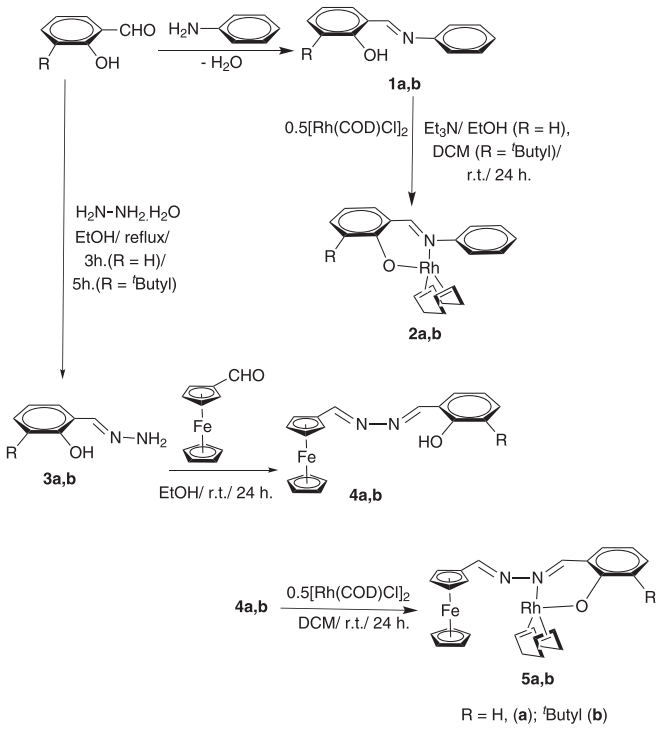
3 | RESULTS AND DISCUSSION

3.1 | Synthesis and characterisation of ligands (1a and 1b)

The *N*-phenylsalicylaldimine ligands **1a** and **1b** were synthesised through Schiff base condensation reactions of the respective aldehydes with aniline, according to previously reported procedures.[26] These were characterised fully using various spectroscopic and analytical techniques. The ^{1}H NMR spectra show the imine proton signals at 8.65 and 8.67 ppm for **1a** and **1b**, respectively. The hydroxyl protons are observed at 13.28 ppm (**1a**) and 14.08 ppm (**1b**), and all aromatic protons appear in their characteristic region for both compounds. The FT-IR spectra further confirm the formation of the two ligands (**1a** and **1b**) through the characteristic strong imine ν(C=N) absorption bands at 1614 and 1610 cm^{-1}, respectively. Also observed in the FT-IR spectra are absorption bands at 2870 and 2954 cm^{-1} corresponding to the ν(O−H) stretching frequencies of **1a** and **1b**, respectively. This is in agreement with the data reported by Hager *et al.*[26]

3.2 | Synthesis and characterisation of Rh(I) mononuclear complex (2a and 2b)

The mononuclear complexes **2a** and **2b** were synthesised by deprotonation of ligands **1a** and **1b**, respectively, with triethylamine, and subsequent complexation with half molar equivalent of the Rh(I) dimer $[RhCl(COD)]_2$ (Scheme 1). Both complexes were isolated as yellow solids in good yields (*ca* 80%). The structural integrity of the complexes was ascertained using elemental analysis, ^{1}H NMR, $^{13}C\{^1H\}$ NMR and FT-IR spectroscopies as well as mass spectrometry. The ^{1}H NMR spectra of both complexes do not show the phenolic proton of **1a** and **1b**, indicating abstraction of the proton by triethylamine so as to facilitate coordination of the ligand to the metal in a bidentate manner. Upon coordination, the imine proton signals of each compound are observed to shift upfield, that is, from 8.65 to



SCHEME 1 Outline of the preparation of aryl- and ferrocenyl-derived complexes (**2** and **5**)

7.98 ppm in the case of **2a**, and from 8.67 to 8.03 ppm in the case of **2b**. This may be explained by the shielding effects from an increased electron density around the imine functionality, which emanates from the back-donation of electrons from the rhodium metal centre to the coordinating imine nitrogen. The spectra also show splitting of the signals for the olefinic COD protons, a phenomenon attributed to the asymmetric environment induced by the chelating *N*,*O*-bidentate ligand. This has been reported for similar compounds.[26,59] The exo- and endo-methylene protons appear upfield as two multiplets, each integrating for four protons. The splitting of the signals is explained by the *trans* effects on proton resonances due to the coordinating *N*,*O*-bidentate ligand.

FT-IR spectroscopic data substantiate the formation of the complexes. The spectra show a shift of the imine absorption band to lower frequency upon coordination of the ligand to the metal, from ν(C=N) = 1614 cm^{-1} (**1a**) and 1610 cm^{-1} (**1b**), to ν(C=N) = 1603 cm^{-1} (**2a**) and 1595 cm^{-1} (**2b**), respectively. The observed shifts are attributed to the weakening of the C=N bond character as a result of back-donation of electrons from the rhodium metal through synergic effects. Such shifts have been reported for similar compounds.[25–27,60] The mass spectral data are consistent with the proposed structures of the complexes by displaying base peaks for the parent $[M]^+$ ions at m/z = 407.04 (**2a**) and 463.14 (**2b**). Elemental analyses results are in agreement with the proposed structures of **2a** and **2b**.

3.3 | Synthesis and characterisation of Hydroxysalicylaldimine compounds (3 and 4)

The hydrazone-based salicylaldimine ligands **3a** and **3b** were prepared by the Schiff base condensation reactions of the respective aldehydes with hydrazine monohydrate (Scheme 1). The ligands were isolated as yellow solids in moderate yield, and characterised fully using various analytical and spectroscopic techniques. These hydroxysalicylaldimine ligands were further reacted through Schiff base condensation reactions with ferrocenecarboxaldehyde in ethanol (Scheme 1). The complexes were isolated as red solids in good yield (79%, **4a**; 89%, **4b**). The ^{1}H NMR spectra of the complexes show the presence of two imine proton signals as singlets at 8.68 and 8.55 ppm for **4a**, and 8.69 and 8.58 ppm for **4b**. The protons on the monosubstituted cyclopentadienyl ring are observed as two broad signals in the ^{1}H NMR spectra of **4a** and **4b**. Typically, these protons resonate as a doublet or triplet but this could not be observed on the given NMR timescale. This is similar to the observation in related but sulfonated compounds previously reported in the literature.[60] The protons of the unsubstituted cyclopentadienyl ring of the ferrocenyl moiety are observed as broad singlets at 4.26 ppm in the ^{1}H NMR spectra of both complexes. The imine carbon signals are observed in their characteristic regions in the ^{13}C{^{1}H} NMR spectra of both complexes (at 163.8 and 162.6 ppm for **4a**, and 163.5 and 163.5 ppm for **4b**). All the other aromatic proton and carbon signals are observed in their characteristic regions in the ^{1}H NMR and ^{13}C{^{1}H} NMR spectra of the complexes. The FT-IR spectrum of each complex exhibits characteristic strong and broad ν(C=N) bands, each with a shoulder assigned to the second imine. The mass spectral data further confirm the formation of the complexes by displaying base peaks for $[M]^+$ ions at m/z = 331.98 and 338.09, corresponding to the molecular weights of **4a** and **4b**, respectively. Elemental analysis (C, H and N) of **4a** and **4b** corresponds to the calculated values.

3.4 | Synthesis and characterisation of Ferrocenylimine–Rh(I) Heterobimetallic complexes (5a and 5b)

The heterobimetallic complexes **5a** and **5b** were synthesised by deprotonating **4a** and **4b**, respectively, with the base triethylamine in dichloromethane, and subsequent reaction with the Rh(I) precursor $[RhCl(COD)]_2$ (Scheme 1). The complexes were isolated as brown solids in good yield (98%, **5a**; 73%, **5b**). The ^{1}H NMR spectra of both heterobimetallic complexes **5a** and **5b** do not display a signal corresponding to the hydroxyl proton, confirming deprotonation of **4a** and **4b**. Subsequent coordination to the Rh(I) precursor is evident in the ^{1}H NMR spectra of **5a** and **5b** through a shift of the imine proton signals of **4a** (from 8.68 to 7.85 ppm, and 8.55 to 7.65 ppm) and **4b** (from 8.69 to 7.87 ppm, and 8.58 to 7.68 ppm), respectively. This is due

to increased electron density around the imine functionality, as explained for **2a** and **2b**. The signals for the monosubstituted cyclopentadienyl ring protons are observed as triplets for both **5a** and **5b**. All the other aromatic protons are accounted for in their characteristic region in the ^{1}H NMR spectra of the complexes. The olefinic as well as the exo- and endomethylene protons of COD show similar behaviour as in **2a** and **2b**, appearing as broad signals in the ^{1}H NMR spectra of **5a** and **5b**. The ^{13}C{^{1}H} NMR spectra, as well as the 2D-NMR experiments (HSQC and COSY), support the formation of the heterobimetallic complexes. The mass spectral data corroborate the proposed structures of **5a** and **5b** by showing molecular ion peaks $[M - Rh(COD) + H]^+$ at $m/z = 332.05$ for **5a** and $[M]^+$ at $m/z = 598.08$ for **5b**. The fragmentation pattern for **5a** is similar to the pattern observed in similar compounds previously reported in the literature.[60]

3.5 | Single-Crystal X-ray diffraction analysis

Crystals suitable for single-crystal X-ray diffraction for **2a** were obtained by the slow evaporation of **2a** in ethanol. Single crystals for **5a** were grown by the slow diffusion of ethanol into a solution of **5a** in dichloromethane. Compound **2a** crystallises in the triclinic space group $P\bar{1}$ with two independent molecules per asymmetric unit (labelled A and B in Figure 1a), whilst compound **5a** crystallises in the monoclinic space group $P2_1$ with one molecule of **5a** and one dichloromethane solvent molecule per asymmetric unit (Figure 1b). No classic hydrogen bonds were found by PLATON for either structure. In both compounds the imine bonds (C=N) are found to be *anti* with the aryl moieties in compound **2a** rotated by *ca* 90° with respect to each other, and this is similar to the data previously reported in the literature for similar compounds.[25,27] Crystal data and selected bond lengths are given in Tables 1 and 2, respectively.

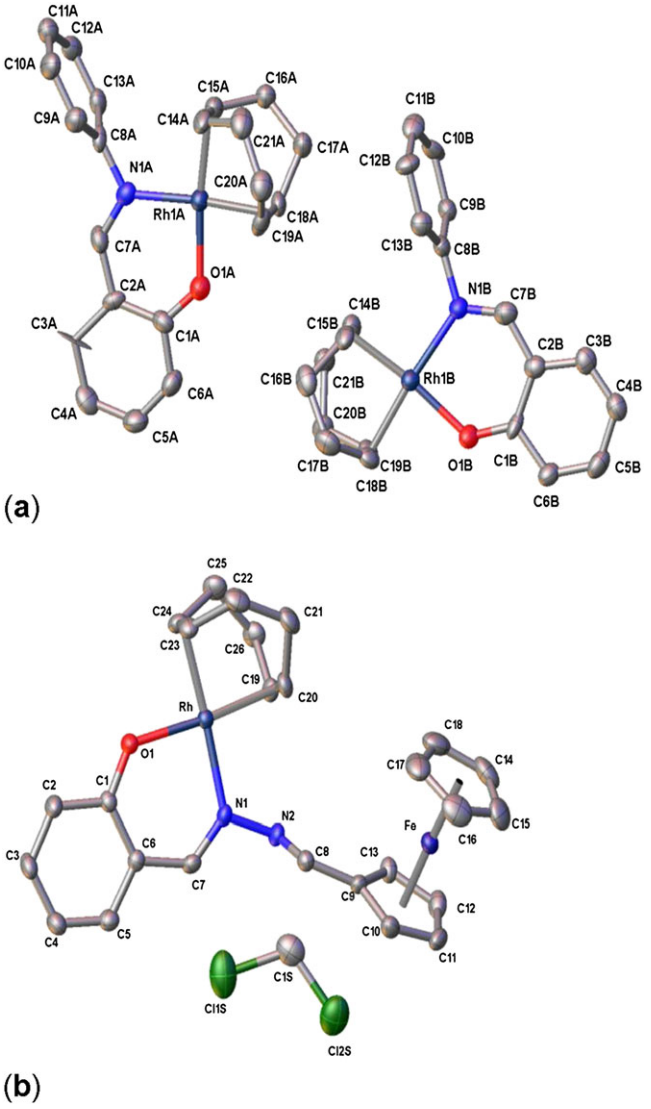


FIGURE 1 Asymmetric units of (a) compound **2a** and (b) compound **5a**. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at the 50% probability level

3.6 | Hydroformylation of 1-Octene

The mononuclear (**2a**, **2b**, **4a** and **4b**) and the heteronuclear (**5a** and **5b**) complexes were evaluated as catalyst precursors in the monophasic (toluene) hydroformylation of 1-octene. The reaction conditions of this study were based on the previously reported conditions for the hydroformylation of 1-octene using analogous ferrocenylimine–Rh(I) catalyst precursors bearing *N*,*O*-bidentate ligands.[60] A catalyst precursor (metal) loading of 2.87×10^{-3} mol% was used based on a 1:2500 (catalyst-to-substrate) ratio. All the experiments were performed in triplicate, and the reported values represent the mean of each experiment. The catalytic data reported in this work were benchmarked against the Rh(I) monomeric[26] and the ferrocenylimine–Rh(I) heterobimetallic[60] catalyst precursors that we have previously reported.

The mononuclear complexes **4a** and **4b** prepared herein are inactive in the hydroformylation of 1-octene under the conditions of 95°C, 40 bar ($CO–H_2$, 1:1) in toluene (5 ml). The Rh(I) monomeric complexes **2a** and **2b** and the heteronuclear complexes **5a** and **5b** show excellent activity and conversion of 1-octene to aldehydes (>300 h^{-1} and >99%, respectively) (Table 3). The observed activity for all the catalyst precursors (**2a**, **2b**, **5a** and **5b**) is consistent with the literature for similar complexes bearing *N*,*O*-bidentate ligands.[25,26,60] Various phosphine-modified heterobimetallic complexes of ferrocene and rhodium have been reported in the literature, and they exhibit improved catalytic activity over their mononuclear counterparts in the hydroformylation of olefins.[52,53,61] The heterobimetallic catalyst precursors bearing *N*,*O*-bidentate ligands in this study show activity comparable to that of their monometallic counterparts.

Interesting to note is the outstanding chemoselectivity for aldehydes, exhibited by the absence of isomerisation products (*cis* and *trans* isomers of 2-octene and 3-octene)

TABLE 1 Crystal data for compounds **2a** and **5a**

	2a	5a
Chemical formula	$C_{21}H_{22}NORh$	$C_{27}H_{29}Cl_2FeN_2ORh$
Formula weight	406.30	627.18
Temperature (K)	173(2)	173(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1$
a (Å)	11.3599(5)	11.533(2)
b (Å)	12.0416(5)	9.945(2)
c (Å)	14.2457(5)	11.850(2)
α (°)	73.363(2)	90
β (°)	69.226(2)	111.07(3)
γ (°)	69.328(2)	90
Volume (Å^3)	1675.54(12)	1268.2(5)
Z	4	2
D_c (g cm^{-3})	1.615	1.642
μ (mm^{-1})	1.026	1.457
F(000)	832	636
Crystal size (mm^3)	0.14 × 0.14 × 0.12	0.24 × 0.14 × 0.12
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
θ min., max. (°)	3.678 to 49.424	3.684 to 54.93
Reflections collected	42 213	5781
Independent reflections	5714	5781
Goodness-of-fit on F^2	1.287	1.125
Final R indexes [$I \geq 2\ s\ (I)$]	R_1 = 0.0531, wR_2 = 0.1129	R_1 = 0.0247, wR_2 = 0.0519
Largest diff. Peak/hole (e Å^{-3})	3.10/−1.22	0.92/−0.47

from all catalyst precursors tested in this work. In our previous work involving the hydroformylation of 1-octene (in biphasic media) using similar catalyst precursors and test conditions,[26,60] we reported good catalytic activity, though characterised by the formation of isomerisation products. In both cases,[26,60] the isomerisation products were ascribed partly to the *in situ* formed nanoparticles from the catalyst in the biphasic media. However, in this work no black particulate matter (nanoparticles) is observed, which would explain the absence of the isomers. Mercury poisoning experiments carried out using catalyst precursor **5a** (Table 3, entry 5) attest to the absence of nanoparticles, as shown by the comparable results. Moreover, the catalyst precursors evaluated in this work could be more stable in a monophasic environment, and not susceptible to change in the actual active species as may be the case in the previously reported aqueous biphasic system (wherein promotion of isomerisation was observed).

The regioselectivity of both the monometallic (**2a** and **2b**) and the heterobimetallic (**5a** and **5b**) catalyst precursors is inclined towards branched aldehydes, with an average percentage ratio of 60:40 (branched-to-linear) (Table 3). Formation of the branched aldehydes during hydroformylation occurs via the Markovnikov insertion.[62] The higher percentage of branched aldehydes could also be as a result of the hydroformylation of isomerisation products to branched aldehydes in the monophasic experiments, further explaining the absence of the isomers in the products. The presence of

TABLE 2 Selected bond distances (Å) for compounds **2a** and **5a**

Bond distance	2a	Bond distance	5a
Rh1A–O1A	2.027(8)	Rh–O1	2.035(3)
Rh1A–N1 A	2.079(9)	Rh–N1	2.054(3)
Rh1A···Cg(C18A/C19A)	2.019	Rh···Cg(C19/C20)	1.996
Rh1A···Cg(C14A/C15A)	2.004	Rh···Cg(C23/C24)	2.2029
Rh1B–O1B	2.027(7)	Fe···Cg(C9/C10/C11/C12/C13)	1.645
Rh1B–N1B	2.097(9)	Fe···Cg(C14/C15/C16/C17/C18)	1.646
Rh1A···Cg(C18B/C19B)	2.024		
Rh1A···Cg(C14B/C15B)	2.004		

TABLE 3 Hydroformylation of 1-octene with catalyst precursors (**2a**, **2b**, **5a** and **5b**) at 8 h[a]

			Aldehydes (%)			*n*/iso	
Entry	Complex	Conv. (%)	Total aldehydes	Nonanal	Branched		TOF (h^{-1})[b]
1	**2a**	99.9	99.9	41.93	58.07	0.72	312.5
2	**2b**	99.9	99.9	41.24	58.76	0.70	312.5
3	**5a**	99.9	99.9	39.92	60.08	0.66	312.5
4	**5b**	99.9	99.9	40.77	59.23	0.69	312.5
5[c]	**5a**	99.9	99.9	43.00	57.00	0.75	312.5

[a]Reactions carried out with (CO–H_2) (1:1) at 40 bar, 95°C in toluene (5 ml) with 7.175 mmol of 1-octene and 2.87 × 10^{-3} mmol of Rh catalyst. GC conversions obtained using *n*-decane as an internal standard in relation to authentic standard iso-octenes and aldehydes.

[b]TOF = (mol product/ mol cat.) h^{-1} and is based on total aldehydes produced.

[c]Mercury poisoning experiment.

the bulkier *tert*-butyl substituent has been previously reported to influence the regioselectivity towards linear aldehydes in the hydroformylation experiments using catalyst precursors bearing *N*,*O*-bidentate ligands.[25,26,60] However, the steric effects of the *tert*-butyl substituent were not as pronounced in this work, as evidenced by the low *n*-to-iso ratios (*ca* 0.70).

4 | CONCLUSIONS

A series of monometallic and heterobimetallic complexes based on *N*,*O*-chelating ligands were synthesised and isolated in good yields. These complexes were characterised using various analytical and spectroscopic techniques, and they are stable at room temperature. The catalytic potential of the complexes was evaluated in the monophasic hydroformylation of 1-octene at 95°C and 40 bar. The ferrocenylimine mononuclear catalyst precursors (**4a** and **4b**) were inactive in the hydroformylation experiments. The Rh(I) mononuclear (**2a** and **2b**) and the ferrocenylimine–Rh (I) heterobimetallic (**5a** and **5b**) complexes showed excellent and comparable catalytic activity in the hydroformylation of 1-octene. These active catalyst precursors also registered remarkable chemoselectivity towards aldehydes, with no side products (isomers) observed. Overall, the presence of the ferrocenyl framework linked to Rh(I) via a bis-imine spacer for monophasic hydroformylation of 1-octene is comparable (activity and regioselectivity) to the data reported for similar compounds in a biphasic medium.[60] A rigid aryl spacer between the ferrocene and the rhodium metal centre may allow ferrocene to influence the electronic properties of the catalytic active species and improve on the efficiency of the heterobimetallic complexes.

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