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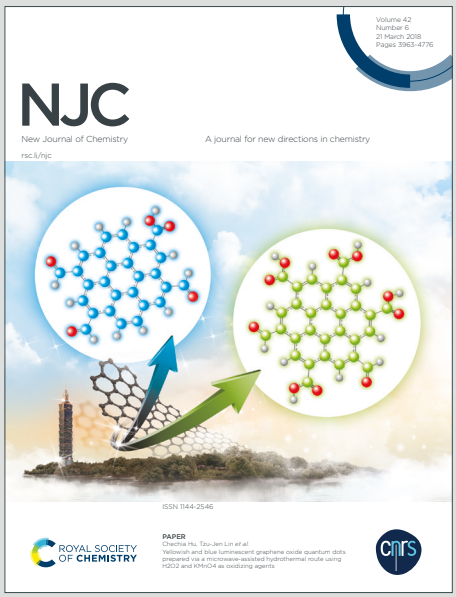

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Catalytic isomerization-hydroformylation of olefins by rhodium salicylaldimine pre-catalysts

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Abstract

A series of new Schiff-base rhodium(I) water-soluble complexes (**C1**-**C3**), were prepared and characterized. These complexes served as catalyst precursors for the hydroformylation of 1-octene and resulted in excellent substrate conversions (>98%) with 100% chemoselectivities to aldehydes, under mild conditions. Notably, good regioselectivities towards branched aldehydes were observed clearly demonstrating the catalysts' ability in thermodynamically favoured isomerization followed by hydroformylation (n/iso ratio ranging between 0.7-1.2). Interestingly, catalyst **C1** uniquely promoted contra-thermodynamic isomerization of 2-octene to 1-octene with up to 50% conversion. The efficacy of catalyst **C1** was further evaluated in the hydroformylation of longer chain olefins (C_{10}-C_{12}), methyl acrylate, ethyl acrylate and styrene. The catalyst displayed conversions >99% with the long chain substrates and much lower conversions with the acrylates. These water-soluble (pre)catalysts were recycled up to three times with no significant loss in catalytic activity and selectivity. Mercury poisoning tests were conducted and the experiments revealed that the conversion of the substrates into aldehydes was due to molecular active catalysts and not as a result of colloidal particles that could have formed in situ through the decomposition of the catalyst precursor. Finally, the molecular catalyst responsible for activity was established using preliminary computational calculations.

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Keywords: isomerization-hydroformylation, rhodium-catalysed, aqueous-biphasic, green chemistry; catalyst recycling; 1-octene.

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Introduction

The hydroformylation (oxo) reaction is an important transition metal-catalysed reaction that converts olefins to aldehydes in the presense of syngas. The first hydroformylation catalysts were cobalt based, and operated at 200 to 450 bars pressure and at temperatures between 140 ˚C and 180 ˚C. It was later discovered that rhodium catalysts were better, since they had the unique ability to catalyse the reaction at low temperature and pressure.[1–5]Aldehydes produced in this process are used in the production of detergents, fragrances and solvents. These aldehydes are also important starting materials for the preparation of a wide range of phamaceuticals, fine chemicals and agrochemicals. Over 90% of the world‘s demand for oxo chemicals comes from Europe, Asia and North America as reported in 2012. [2,6-10]

Rhodium is the most active metal for catalysing this reaction but the challenge is that it is a very expensive metal. As a result, researchers in academia and industry have come up with various approaches to recover this precious metal during catalysis. Biphasic approaches have been explored. In this approach, the catalyst is immobilised in one of the phases whilst the substrate and products are contained in the other phase. This allows easy recovery of the expensive catalyst from the products and hence the recovered catalyst can be reused in another catalytic cycle. Such systems include combinations of water with either organic solvent, fluorous solvent or ionic liquids with organic solvent. Apart from that approach, catalysts may be immobilised on a solid support which results in a heterogeneous catalytic system. [10-20]

The aqueous biphasic hydroformylation reaction has been successfully conducted on an industrial scale in the RuhrChemie/Rhone-Poulenc process (OXEA Process).[2,21-22] In this system, a Rh/TPPTS catalyst is employed. The advantage of this system is that it employs water, which is considered a green solvent because it is non-toxic, non-flammable, easily accessible and a cheap alternative that is readily available.[23] The aqueous biphasic hydroformylation of olefins has been widely explored with short chain olefins and poor solubility of the longer chain substrates results in suppressed catalytic activities.

In light of this, we developed new water-soluble organometallic complexes and evaluated their efficacy as catalyst precursors for aqueous biphasic hydroformyaltion of long chain olefins (C_8-

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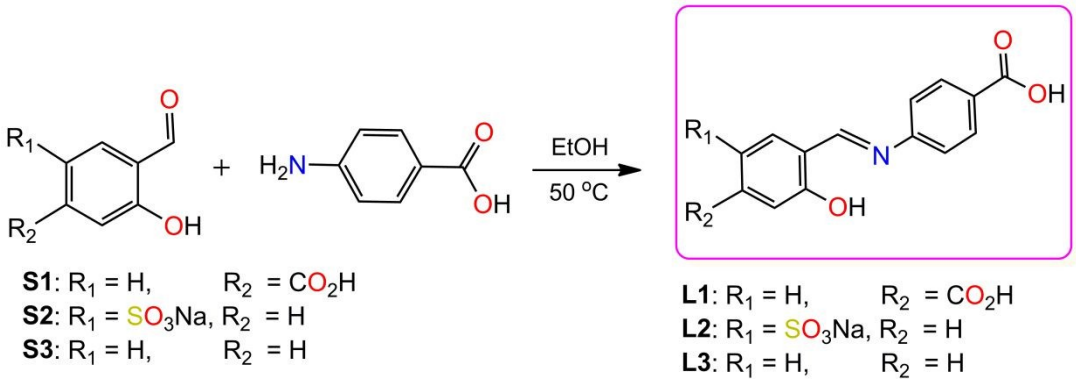
C_{12}). We also extended the study to acrylates and styrene as substrates, and further investigated catalyst recyclability and stability.

Results and discussion

*Synthesis and characterization of ligands **L1** and **L2***

Ligands (**L1-L3)** were synthesised by reacting substituted salicylaldehydes with 4-aminobenzoic acid (**Scheme 1**) with 4-aminobenzoic acid. In order to prepare **L2**, the sulfonated salicylaldehyde precursor was first prepared according to a protocol reported in literature.[24] Ligands **L1** - **L3** were obtained as yellow to orange solids in relatively good yields of between 64-89%, and are highly thermally stable (melting points in the range of 195 ˚C to 304 C˚. Furthermore, the ligands **L1** and **L2** are insoluble in common solvents (toluene, MeOH, EtOH, DCM, EtOAc) at room temperature but dissolved readily in water at ≥ 65 ˚C. This may be due to better hydrogen bonding interactions between the carboxylic acid functional group of the ligands and water at temperatures above 65 ˚C.



S1: R_1 = H, R_2 = CO_2H
S2: R_1 = SO_3Na, R_2 = H
S3: R_1 = H, R_2 = H

L1: R_1 = H, R_2 = CO_2H
L2: R_1 = SO_3Na, R_2 = H
L3: R_1 = H, R_2 = H

Scheme 1: Outline for the synthesis of **L1-L3**.

The ^{1}H NMR spectra of **L1**–**L3** display expected imine proton signals upfield in the region of ≈ 9.0 ppm. The aromatic proton signals in these ligands are seen in the region of 6.73 to 8.02 ppm. Notably, the aromatic protons of the *para*-substituted phenyl ring appear as two doublets integrating for 2 protons each in all the ligands. The carboxylic acid and phenolic proton signals were not always seen in the ^{1}H NMR spectra, possibly due to the deuterated solvent used, however the phenolic and carboxylic acid protons in **L1** and **L3** gave rise to singlets at 12.55 ppm (**L1**, O*H*) and 12.71 ppm (**L3**, O*H*) and 12.95 (**L3**, COO*H*) ppm.

The ^{13}C{^{1}H} NMR spectra of ligands **L1** – **L3** all are similar and display all expected signals. The carbonyl carbon of the carboxylic acid groups (COOH) appears downfield in the region of ≈

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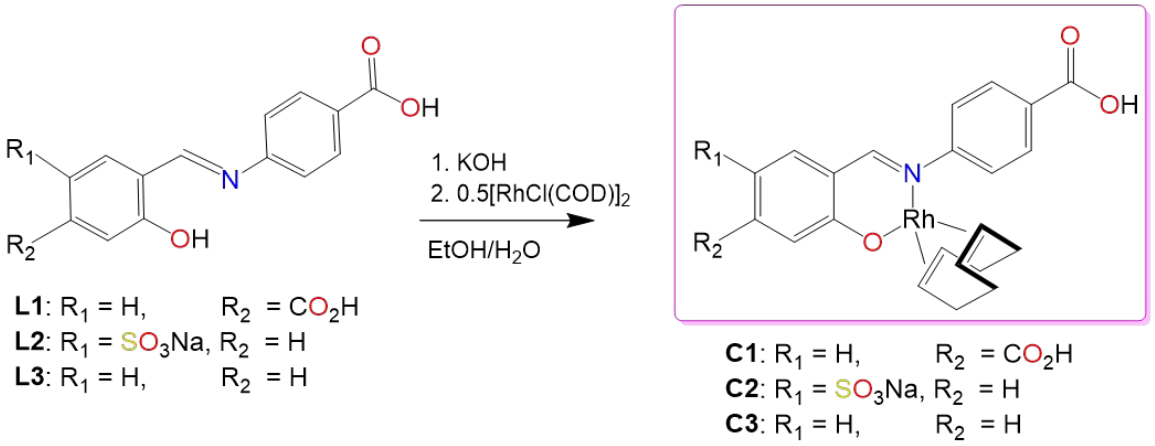
167 ppm for all the ligands. Slightly upfield to this are the imine (C=N) carbon signals, which resonate at ≈ 160 ppm. The aromatic carbon signals are seen in the region of 113.01 ppm to 134.30 ppm. The carbon signal directly bonded to the oxygen atom of the phenol group is more deshielded than the other aromatic carbon signals and resonates at 153.60 ppm (**L1**), 153.10 ppm (**L2**) and 153.61 ppm (**L3**).

The high resolution electrospray ionisation mass spectra results for ligands **L1 - L3** validated the integrity of the ligands by displaying fragmentation peaks at *m/z* = 285.0633 (**L1**, $[M+H]^+$), *m/z* = 317.1280 (**L2**, $[M-Na-2H]^+$), *m/z* = 242.0809 (**L3**, $[M+H]^+$).

*Synthesis and characterization of Rh(I) complexes **C1** – **C3***

The salicylaldimine ligands (**L1-L3**) were dissolved in a H_2O/EtOH (1:1) mixture and deprotonated using KOH base for 30 minutes at room temperature. A solution in a ligand/rhodium dimer molar ratio of 2:1 was left to stir at room temperature for 3 hours (**Scheme 2**). The solvent was removed to afford bright yellow to orange water-soluble (4 mg/mL – 5 mg/mL) complexes which were obtained in good yields (of 90% for **C1**, 78% for **C2** and 77% for **C3)**.



Scheme 2: Outline for the synthesis of **C1 - C3**.

In the ^1H NMR spectra of the complexes, the imine protons appear as singlets at around 8.2-8.3 ppm. The evidence of the complex formation was confirmed by the upfield shifts of the imine protons upon coordination to the rhodium metal from the ligands **L1**, **L2** and **L3** (9.03 ppm, 9.00 ppm and 8.98 ppm) respectively to the complexes **C1**, **C2** and **C3** (8.35 ppm, 8.20 and 8.22 ppm) respectively. The aromatic protons of all three complexes were observed at around 7.95 ppm and

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7.32 ppm. The upfield shifts of the imine peaks was caused by the reduction of electron density around the imine functionality and the de-shielding caused by the electron back- donation from the rhodium centre. A split of the olefinic 1,5-cyclooctadiene protons was not observed as expected upon the complexation due to the asymmetric environment induced by the N^O chelating ligand, however, this has also been observed in literature. [24]

The $^{13}C\{^{1}H\}$ NMR spectra of the complexes **C1** – **C3** are similar and show the expected signals. The carbon peaks for the carbons directly bonded to the oxygen of the phenol shifted slightly downfield from around 153 ppm in the ligands to 156 ppm in the complexes. This is partly due to the de-shielding caused by the decreased electron density upon rhodium coordination. There are new signals observed on the spectrum at around ≈ 80 ppm (**C**H COD) and ≈ 30 ppm (**C**H_2 COD) due to the cyclooctadiene's olefinic and alkyl carbons respectively.

The high resolution electrospray mass spectra (ESI-MS) validated the synthesis of the complexes at *m/z* = 497.9933 $[M+3H]^+$ for **C1**, *m/z* = 555.0132 $[M+2H]^+$ for **C2** and *m/z* = 453.2105 $[M+2H]^+$ for **C3** in the positive ion mode for all complexes.

*Single Crystal X-ray structure of **C3***

Complex **C3** was also characterised by single crystal X-ray diffraction. The crystals were obtained by slow diffusion of THF into a concentrated solution of **C3** dissolved in dimethyl sulfoxide. Complex **C3** is shown in **Figure 1** in a ball and stick representation.

The molecular crystal structure of complex **C3** shows a distorted square planar geometry around the Rh metal centre that is coordinated to the N^O-chelating salicylaldimine ligand and the cyclooctadiene moiety. The bond angles around the Rh metal centre range between 82° and 98° which slightly deviate from the 90° angle around the metal for a square planer complex. Similar results have been reported in literature.[16,17] The bond angles around the central carbon atom of the carboxylic acid moiety (C_{22}) are in agreement with the angles for a trigonal planar molecule with all three angles approximately 120°. A THF solvent molecule also co-crystallised with the complex and this has not been included in Figure 1 for clarity. **Table 1** and **Table 2** summarise selected crystallographic data, bond angles and bond angles

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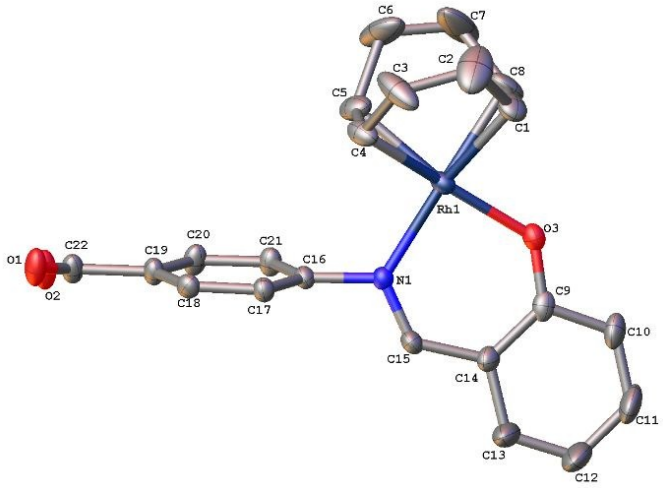

Figure 1. Molecular structure of **C3** determined by single crystal X-ray diffraction. Hydrogen atoms have been omitted in the structure for clarity.

Table 1 Selected bond angles and bond distances for the molecular structure of **C3.**

Bond Lengths (Å)		**Bond Angles (°)**	
Rh1-N1	2.082(5)	N1-Rh1-O3	89.57(17)
Rh1-O3	2.015(4)	N1-Rh1-C4	93.5(2)
Rh1-C1	2.129(6)	N1-Rh1-C5	97.8(2)
Rh1-C4	2.106(6)	O3-Rh1-C1	87.4(2)
Rh1-C5	2.116(7)	O3-Rh1-C8	85.5(3)
Rh1-C8	2.136(6)	C1-Rh1-C4	82.4(3)
C22-O1	1.258(8)	C4-Rh1-C8	96.0(3)
C22-O2	1.282(7)	C19-C22-O1	119.4(5)
N1-C15	1.290(7)	C19-C22-O2	116.9(5)
		O1-C22-O2	123.6(5)

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Table 2 Crystallographic data selected for the molecular structure of **C3**.

	C3
Empirical formula	$C_{23.5}H_{22}NO_{3.5}Rh$
Formula weight	477.33
Temperature/K	100 (2)
Crystal system	monoclinic
Space group	C2/c
a/Å	37.918(5)
b/Å	6.9343(9)
c/Å	16.008(2)
α/°	90
β/°	102.150(3)
γ/°	90
Volume/Å^3	4114.9(9)
Z	8
ρ_{calc}g/cm^3	1.541
μ/mm^{-1}	0.857
Crystal description,colour	Block, Red
Crystal size/mm^3	0.857 × 0.205 × 0.072
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.2 to 56.82
Index ranges	$-50 \le h \le 49$, $-9 \le k \le 9$, $-21 \le l \le 21$
Nref	5139
Independent reflections	5161 [R_{int} = 0.0480, R_{sigma} = 0.0311]
Data/restraints/parameters	5161/0/243
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0714, wR_2 = 0.2160
Final R indexes [all data]	R_1 = 0.0811, wR_2 = 0.2286
Largest diff. peak/hole / e Å^{-3}	5.46/-0.75

*Hydroformylation of 1-octene using complexes **C1-C3** as catalyst precursors*

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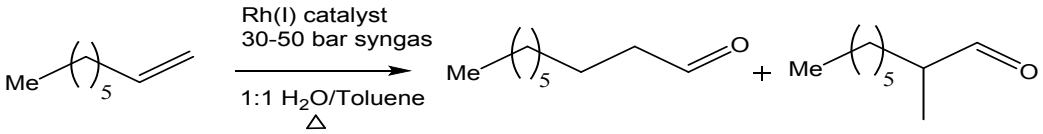
The salicyldamine (**C1-C3**), rhodium(I) complexes were evaluated as catalyst precursors in aqueous biphasic hydroformylation of 1-octene. The reaction of 1-octene with syngas (1:1, CO/H_2) in the presence of a water-soluble Rh(I) catalyst precursor to form a mixture of linear and branched aldehydes and isomerization products (internal olefins) is shown below in **Scheme 3**.



Scheme 3 Aqueous biphasic hydroformylation of 1-octene.

The catalyst precursors **C1-C3** were separately dissolved in 5 mL water, then 1-octene substrate and *n*-decane (internal standard) were dissolved in 5 mL toluene. The two solutions were poured into a stainless steel reactor which was then pressurised and heated to the desired temperature. After the reaction period, the reaction solution was cooled and the organic layer containing the products and unreacted substrate were separated from the catalyst containing aqueous layer by decantation. The organic layer was analysed by gas chromatography. Toluene was chosen since it has been previously used in similar hydroformylation reactions.[25,26] **C3** was used to optimise the reactions.

Conversion as a function of time

At 30 bar and 75 °C, the reactions were set up for 2, 4, 6 and 8 hours. Conversion of 1-octene increases steadily over the time intervals from 30 % conversion at 2 hours, to 78 % at 6 hours. Complete substrate conversion (99 %) was realised at 8 h and no further conversion was observed at 10 h (**Figure 2**), thus 8 h was chosen as the optimum time for the reactions. This kinetic profile is expected, since no induction period is observed and the conversion increases with respect to time up to 100%. This suggests kinetics controlled by mass transfer of the substrate, which is expected for the biphasic hydroformylation of 1-octene.

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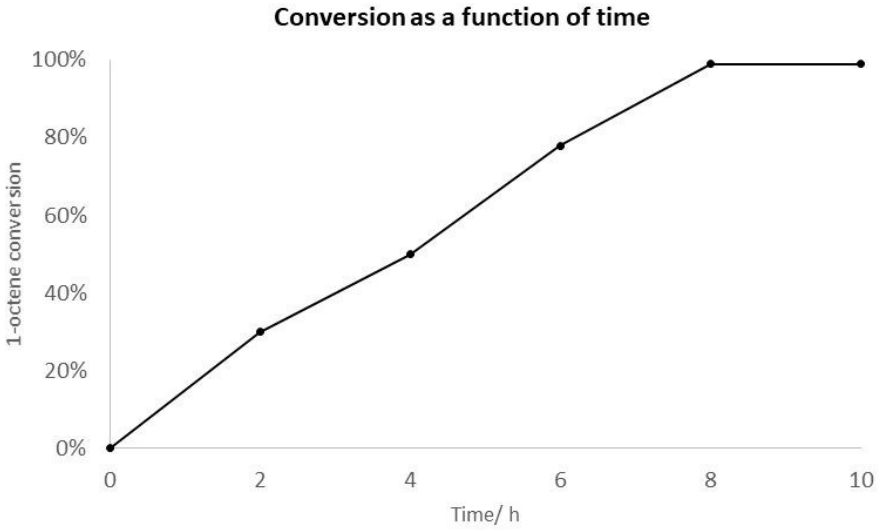

Figure 2 Conversion as a function of time during the hydroformylation of 1-octene by **C3**.

Conditions: Reaction carried out using **C3** as a catalyst precursor (Catalyst loading 1.29 x 10^{-3} g, 2.87 x 10^{-3} mmol), at 30 barss syngas pressure (1:1 ratio of CO:H_2), and 75°C, in H_2O (5 mL) and toluene (5 mL), with 1-octene (0.721 g, 6.37 mmol) and *n*-decane internal standard (0.180 g, 1.26 mmol) over 8 hours. The reactor was flushed with nitrogen thrice, followed by flushing twice with syngas prior to beginning the reaction. Average error estimate ± 0.31 (2 h), ± 0.77 (4 h), ± 0.65 (6 h), ± 0.72 (8 h), ± 0.85 (10 h).

Effect of temperature

At 30 bars and 75 °C (**Table 3**, **Entry 1**) the conversion of 1-octene was excellent. Of the 98 % converted substrate, 78 % aldehydes formed and 22 % products were due to isomerisation of the 1-octene to form *iso*-octenes. The activity of the catalyst was found to be 211 h^{-1}. The catalyst however demonstrates an *n/iso* ratio of 1.2, which means that the catalyst was not very selective to the formation of linear or branched aldehydes. Increasing the temperature to 85 °C (**Table 3, Entry 2**) resulted in similar conversion of 1-octene, however, an increase in aldehydes formed was seen. This increased from 78% at 75 °C to 97% at 85 °C, while the catalyst's activity also increased from 211 h^{-1} to 267 h^{-1}.

This may suggest that the syngas mixture diffuses more readily into the solvents at higher temperatures, thus promoting hydroformylation. The selectivity for linear aldehydes is not favoured at higher temperatures (*n;iso* ratio = 0.6) and this is expected since at higher temperatures (at 85 °C and 95 °C) isomerization is known to dominate and the resultant internal olefins are ultimately hydroformylated to yield mostly branched aldehydes. Therefore, 85 °C was chosen as the optimum temperature and was used for further pressure optimization.

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Table 3 Effect of temperature in hydroformylation of 1-octene using **C3**.

Entry	[a]Temp. (˚C)	[b]Conv. (%)	Aldehydes (%)			*Iso*-octenes (%)	*n:iso*	TON
			Total	linear	branched			
1	75	98	78	56	44	22	1.2	1688
2	85	99	97	39	61	3	0.6	2136
3	95	99	92	39	61	8	0.6	2056

Conditions: Reactions carried out in toluene (5 mL) and distilled water (5 mL) with **C3**, (Catalyst loading (1.29×10^{-3} g, 2.87×10^{-3} mmol), 1-octene (0.721 g, 6.37 mmol) and *n*-decane as an internal (0.180 g, 1.26 mmol) over 8 hours. The reactor was flushed with nitrogen thrice, followed by flushing twice with syngas ($CO:H_2$ = 1:1). Average error estimate ± 0.78 (75˚C), ± 0.69 (85˚C), ± 0.56 (95 ˚C). TON = (mmol of aldehydes/mmol of Rh) and is based on total aldehydes. [a]Temp. = temperature, [b]Conv. = conversion.

Effect of pressure

Pressure optimisations were then carried out at 85 °C. The pressure was varied from 30 bars to 40 bars (**Table 4, Entry 2**). Much like at 30 bars and 85 °C, substrate conversion was 99 %, and this time 1-octene was converted entirely to aldehydes. The reaction was 100 % chemoselective towards aldehyde, while the *n/iso* ratio remained almost constant. Upon increasing the pressure to 50 bars, the substrate conversion dropped slightly to 95 % (**Table 4, Entry 3**), together with a slight drop in chemoselectivity. 10 % *iso*-octenes were observed in this case.

Table 4. Effect of pressure in the hydroformylation of 1-octene using **C3**.

Entry	Pressure (bars)	[a]Conv. (%)	Aldehydes (%)			*Iso*-octenes (%)	*n:iso*	TON
			Total	linear	branched			
1	30	99	97	39	61	3	0.6	2136
2	40	99	100	43	57	0	0.7	2176
3	50	95	90	40	60	10	0.6	1896

Conditions: Reactions carried out in toluene (5 mL) and distilled water (5 mL) with **C3**, (Catalyst loading (1.29×10^{-3} g, 2.87×10^{-3} mmol), 1-octene (0.721 g, 6.37 mmol) and *n*-decane as an internal (0.180 g, 1.26 mmol) over 8 hours. The reactor was flushed with nitrogen thrice, followed by flushing twice with syngas ($CO:H_2$ = 1:1). Average error estimate ± 0.70 (30 barss), ± 0.25 (40 barss), ± 0.67 (barss). TON = (mmol of aldehydes/mmol of Rh) and is based on total aldehydes. [a] Conv. = conversion.

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The TON, determined based on total desired aldehydes, increased on increasing the pressure from 30 bars to 40 bars, but dropped slightly at 50 bars syngas pressure. The increase in CO partial pressure is known to result in increased rates of CO insertion which results in suppressed isomerization rates. However, in this system the CO seems to displace the cyclooctadiene moiety. This results in the formation of a Rh-hydrido carbonyl species which is not a very active hydroformylation catalysts under mild conditions but rather active for the isomerization reaction. Therefore, 40 bar and 85 °C was chosen as the optimum reaction conditions since under these conditions, the 100 % substrate was conversion was achieved with 100 % selectivity to aldehyde.

*Hydroformylation of 1-octene using **C1**–**C3** as (pre)catalysts*

Hydroformylation reactions with catalyst **C1**–**C3** were performed at the optimum conditions of 40 bars, 85 °C and 8 h. The catalysts precursors **C1**–**C3** all displayed excellent catalytic conversions as high as 99 % (**Table 5**). The 1-octene was converted to aldehydes exclusively, and no *n*-octane and *iso*-octenes were formed within the detectable limits of the GC.

The catalyst precursors showed turnover numbers in the range of 2000-2400, with the most water-soluble catalyst precursor (**C2**) exhibiting the highest TON of 2314 followed by **C1** (with a TON of 2208). In general, the less water-soluble the catalyst precursor the lower the TON, suggesting that the catalyst precursor's solubility in water impacts on performance (**Table 5**). The catalyst precursors gave almost equal amounts of branched and linear aldehydes and therefore are not very regioselective.

Table 5 Hydroformylation of 1-octene using **C1-C3** as catalyst precursors.

Entry	**[a]Cat.**	**[b]Conv. (%)**	**Aldehydes (%)**			***Iso*-octenes (%)**	***n:iso***	**TON**
			Total	**linear**	**branched**			
1	**C1**	99	100	43	57	0	0.8	2208
2	**C2**	99	100	53	47	0	1.2	2318
3	**C3**	99	100	43	57	0	0.7	2176

Conditions: Reactions carried out in toluene (5 mL) and distilled water (5 mL) with **C1-C3**, (Catalyst loading (1.29×10^{-3} g, 2.87×10^{-3} mmol) separately. Substrate used was 1-octene (0.721 g, 6.37 mmol) and *n*-decane as an internal (0.180 g, 1.26 mmol) over 8 hours. The reactor was flushed with nitrogen thrice, followed by flushing twice with syngas ($CO:H_2$ = 1:1). Average error estimates: ± 0.21 (**C1**), ± 0.86 (**C2**), ± 0.69 (**C3**). TON = (mmol of aldehydes/mmol of Rh) and is based on total aldehydes. [a]Cat. = catalyst precursor. [b] Conv. = conversion.

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These results are comparable to what has been reported in the literature for similar catalyst precursors.[24,26] **C2** slightly favours the formation of linear aldehydes, whereas, **C1** and **C3** gave slightly more branched than linear aldehydes (**Table 5**). This indicates that the steric bulk around the rhodium is not sufficient to cause a discrimination of the linear over the branched aldehydes and *vice versa.* Introducing a bulky ligand such a water-soluble phosphine such as 1,3,5-triaza-7-phosphaadamantane (PTA), to add to the steric bulk around the rhodium with an aim to fine-tune the regioselectivity and water-solubility of the pre-catalysts. N^N and N^P chelating catalyst precursors have been reported for hydroformylation and they proved to have superior regioselectivity.[26a]

In order to compare the perfomance of the catalysts, the reactions were perfomed under the optimum conditions but instead of a reaction time of 8 hours, the reactions were stopped at 4 hours. The results show that there is significant isomerization activity in the first few hours of the reaction and catalysts favouring the linear aldehyde nonanal in the first four hours. This indicates that the branched aldehydes observed at 8h are as a result of the hydroformylation of 1-octene isomerization products. The results obtained for this study are summarised in Table 6.

Table 6. Hydroformylation of 1-octene using **C1-C3** as catalyst precursors.

Entry	[a]Cat.	[b]Conv. (%)	Aldehydes (%)			*Iso*-octenes (%)	*n:iso*	TON
			Total	linear	branched			
1	**C1**	53	58	44	18	42	2.4	752
2	**C2**	49	55	42	13	45	3.2	748
3	**C3**	50	57	36	21	43	1.7	750

Conditions: Reactions carried out in toluene (5 mL) and distilled water (5 mL) with **C1-C3**, (Catalyst loading (1.29×10^{-3} g, 2.87×10^{-3} mmol) separately. Substrate used was 1-octene (0.721 g, 6.37 mmol) and *n*-decane as an internal (0.180 g, 1.26 mmol) over 4 hours. The reactor was flushed with nitrogen thrice, followed by flushing twice with syngas ($CO:H_2$ = 1:1). Average error estimates: ± 0.32 (**C1**), ± 0.98 (**C2**), ± 0.87 (**C3**). TON = (mmol of aldehydes/mmol of Rh) and is based on total aldehydes. [a]Cat. = catalyst precursor. [b] Conv. = conversion.

The results show that the catalysts have very comparable activity and selectivity. At 4 hours approximately 50% conversion is achieved with isomerization competing effectively with the

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hydroformylation reaction. It is very clear that as the reaction proceeds to 8 h as shown in Table 5, the hydroformylation of internal olefins results in the production of branched aldehydes.

An investigation onto the extent to which these catalytic systems act as isomerization catalysts was inverstigated by subjecting 2-octene under isomerization conditions for 6 hours at 30 bar hydrogen pressure and 120 °C in the presence of hydrogen only using **C1**. Analysis of the reaction mixture showed that 2-octene isomerized to 1-octene (Figure 3).

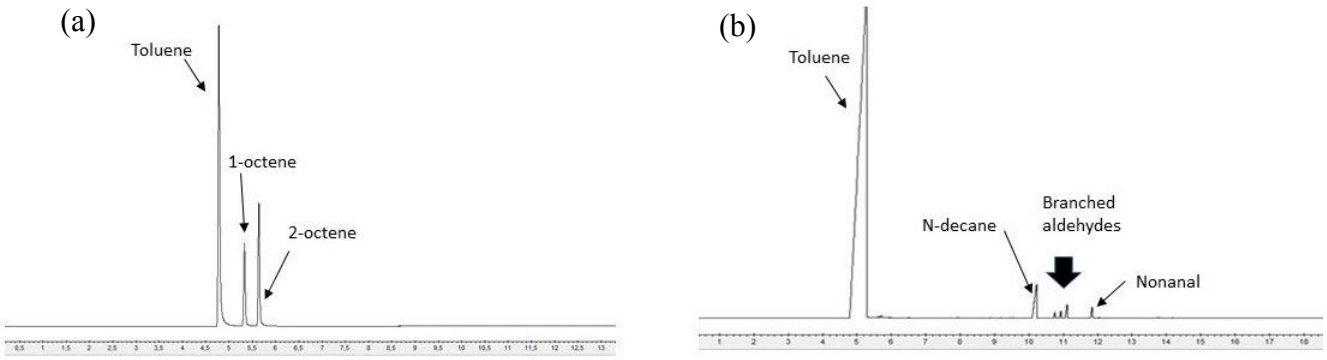

Figure 3. (a) Chromatogram after isomerization of 2-octene and (b) chromatogram after mixure in (a) was hydroformylated.

In the isomerization reaction about 40 % of 2-octene was converted to 1-octene exclusively, showing that the reaction is selective towards formation of the terminal olefin. When this mixture was subjected to the optimized hydroformylation conditions, the same distribution of linear (39%) and branched aldehydes (61%) was observed. This is not a new phenomenon as has been reported by van Leeuwen and Kamer who earlier observed 2-octene to 1-octene isomerization followed by hydroformylation to give mostly nonanal. Furthermore, they attributed contra-thermodynamic isomerization of 2-octene to 1-octene (that evetually leads to *n*-aldehyde selectivity) to be driven by the large bite angles (ranging from 105.7° to 131.2°) in the catalysts' phenoxaphosphino modified xanthene-type ligands. [26b,c] A measurement of the salicylaldimine ligand's N-Rh-O bite angle, in **C1**, gave a significantly smaller value of 89.79°, therefore explaining the observed lower nonanal selectivity in this study.

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Catalyst recyclability

Upon completion of each reaction, the biphasic solutions were separated by decantation then a fresh substrate was introduced to the aqueous layer and the reaction was repeated for recycling studies. Catalysts **C1-C3** can be reused up to three time without significant loss of activity and selectivity (**Figure 4**). On the fourth cycle the catalysts displayed conversions below 10%. Decrease in conversion is an indication that with time the active catalyst leaches into the organic layer.

The ICP-MS experiments were conducted to analyse the organic layer after each cycle. The results show significant leaching of the Rh metal into the toluene layer with 64% (**C1**) and 66% (**C2**) loss of Rh after the first cycle. Catalyst **C3** displayed the most leaching because this catalyst shows some partial solubility in toluene, with 83 % loss observed. In the second and third cycles, further losses were observed with catalyst **C3** showing the least conversion in the 3rd cycle. After this no activity was observed for all catalysts. This may suggest that the water-phase is acting as a reservoir for the active Rh species responsible for the hydroformylation activity.

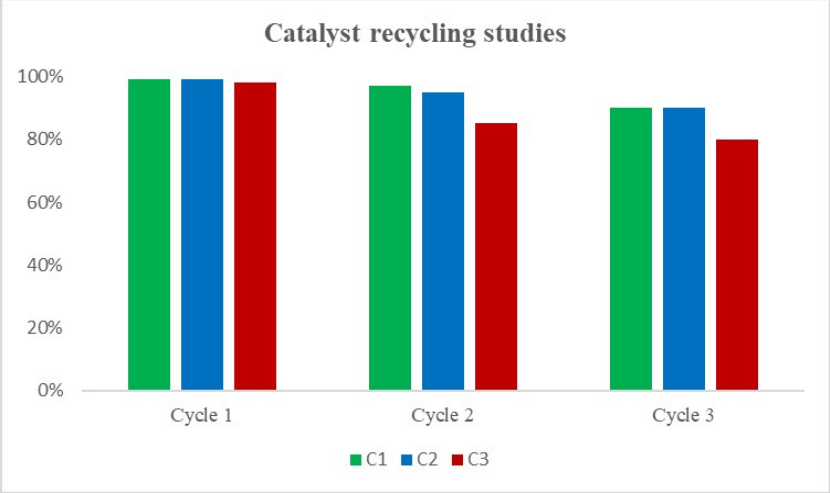

Figure 4 Results obtained after catalyst (**C1–C3**) recyclability studies.

Conditions: Reactions carried out in toluene (5 mL) and distilled water (5 mL) with **C1-C3**, (Catalyst loading (1.29 x 10^{-3} g, 2.87 x 10^{-3} mmol) separately. Substrate used was 1-octene (0.721 g, 6.37 mmol) and *n*-decane as an internal (0.180 g, 1.26 mmol) over 8 hours. The reactor was flushed with nitrogen three times, followed by flushing twice with syngas ($CO:H_2$ = 1:1).

Mercury Poisoning Tests

A homogenous catalyst, can form heterogeneous metal film strips, metal powders and metal nano-particles which end up catalysing the reactions, instead the molecular catalysts.[27-28] The

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presence of Hg(0) around metal nano-particles forms amalgams which then retard the metal's ability to perform catalytic conversions. This tool is used to distinguish true homogenously catalysed reactions from those catalysed by metal nano-particles.[29]

In separate experiments, the hydroformylation reactions were conducted with a drop of mercury (in addition to all necessary inputs such as the substrate, catalyst precursor, internal standard, syngas and a solvent). The reaction was carried out, and after 8 h the aqueous and organic layers were separated and the organic layers were analysed by GC. The catalyst's activity, chemoselectivity and regioselectivity were similar to the reactions done in the absence of the mercury (**Figure 5**), this proved that molecular homogenous catalysts are responsible for the hydroformylation of 1-octene.

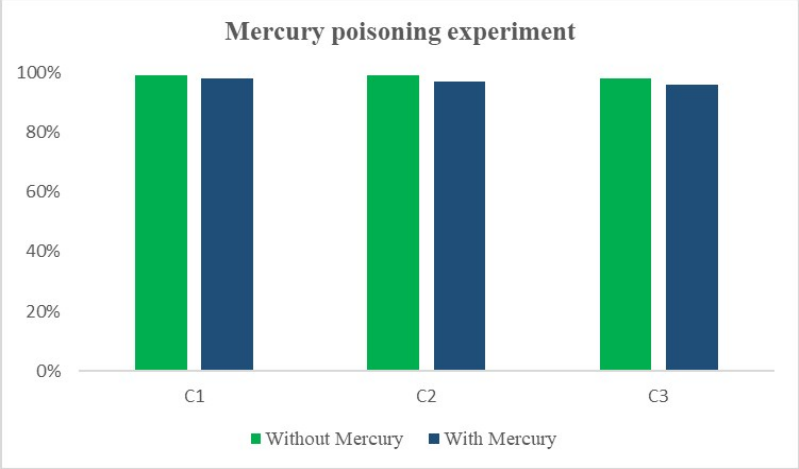

Figure 5 Mercury poisoning experiments.

Conditions: Reactions carried out in toluene (5 mL) and distilled water (5 mL) with **C1-C3**, (Catalyst loading (1.29 x 10^{-3} g, 2.87 x 10^{-3} mmol) separately. Substrate used was 1-octene (0.721 g, 6.37 mmol) and *n*-decane as an internal (0.180 g, 1.26 mmol) over 8 hours. The reactions done with Hg(0) had a few drops of metallic mercury added, and reactor was flushed with nitrogen three times, followed by flushing twice with syngas ($CO:H_2$ = 1:1).

Preliminary modelling of the active catalyst

The pathway was modelled (computed) and investigated using Spartan '10 V1.1.0 Molecular Modelling Program at Semi-Empirical PM3 (D) level at 1 atm and 298.15 K in order to simulate the experimental conditions. The PM3 (D) method has been specifically parameterized for transition metal systems for quick exploratory calculations on trends.[30,31]

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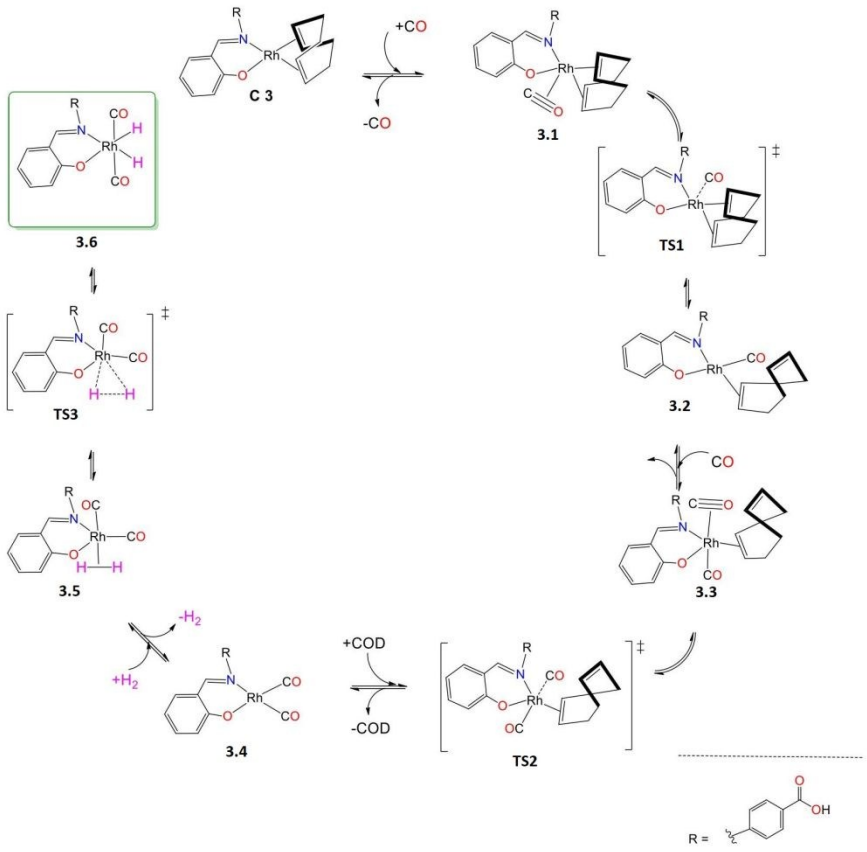
It has been reported that a Rh-hydride species formed *in situ* is the active catalyst.[32-33] Since 1,5-cyclooctadiene (COD) is a good leaving group, it was assumed that in the presence of excess syngas, it is initially displaced by carbon monoxide and hydrogen to form a dicarbonyl, dihydride species, as observed by Ramarou *et al*. in the synthesis of Rh carbonyl complexes.[34a] The reaction pathway is considered to go through 3-centred concerted addition mechanism across a square planar complex to generate a dihydride active species. The first step towards the generation of the active species involves the coordination of carbon monoxide to the pre-catalyst to form an intermediate (**3.1**) (**Scheme 4**).[34b]



Scheme 4. Possible reaction pathway for generation of catalytically active species.

After the formation of 5-coordinate intermediate, the first transition state (**TS1**) is achieved. In this transition state one Rh-olefin bond dissociates as a new Rh-CO is formed in intermediate (**3.2**). This leaves a vacant site for coordination of a second CO molecule to give intermediate (**3.3**). As the second CO ligand begins to coordinate to the rhodium centre *via* a σ-bond, the second Rh-olefin bond (of the COD ligand) dissociates in transition state (**TS2**). This results in the expulsion of COD

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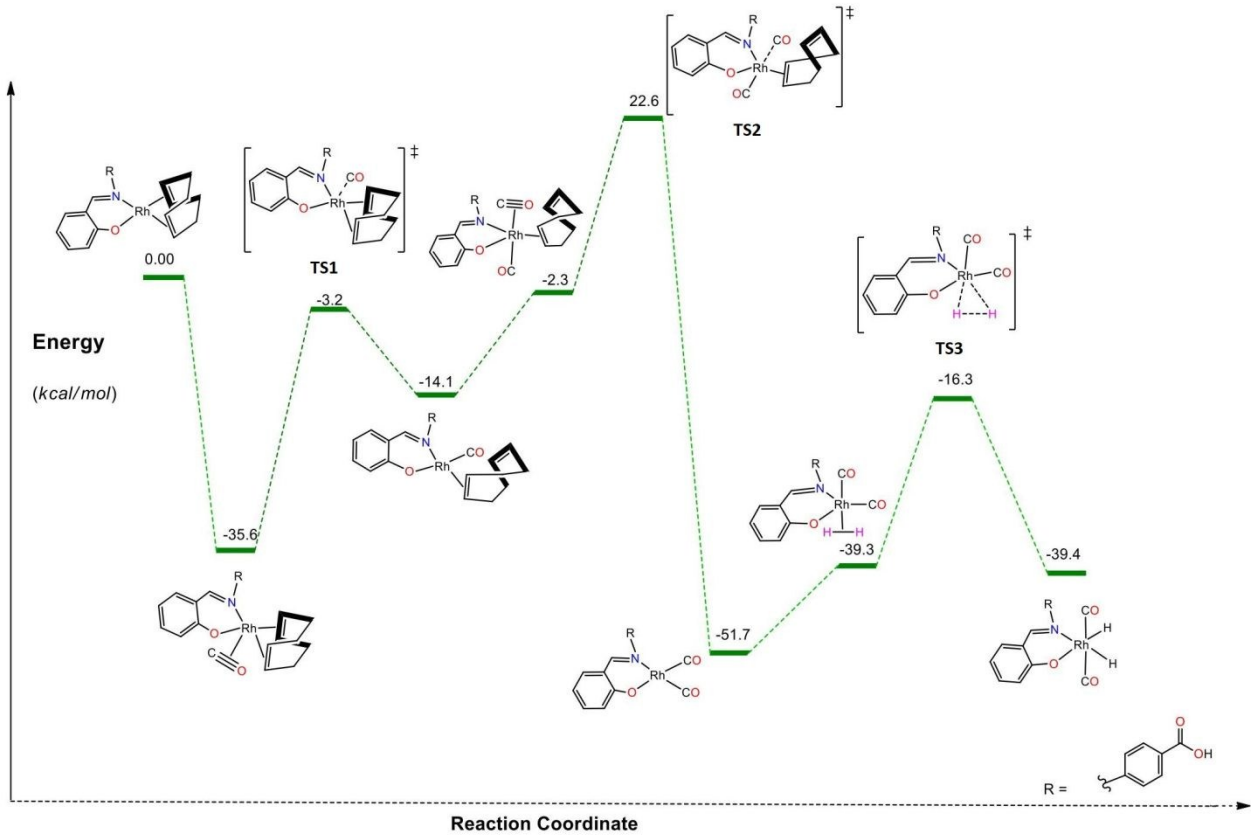
and the formation of a 4-coordinate square planar intermediate (**3.4**). The process from **3.3** to **3.4** overcomes an energy barrier of 24.9 kcal/mol. Intermediate **3.4** then associates with a molecule of H_2 in the next step to afford an intermediate with a Rh-H_2 bond (**3.5**). Intermediate **3.5** may exist in an equilibrium with the species (**3.6**) which is formed *via* a transition state **TS3**. Reaction energy profile for the possible pathway towards the formation of the active species **3.6** is shown in **Scheme 5**.



Scheme 5. Reaction energy profile for the third possible pathway for the formation of the active species.

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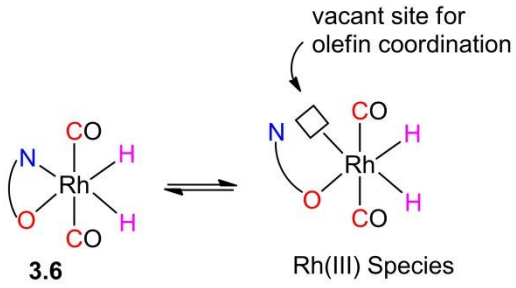
The hydroformylation of olefins mechanism has been extensively studied over the years and it is generally accepted that a Rh(I) is the catalytically active species. Though rare, Rh(III) has been found to promote hydroformyaltion in a some ocassions. [34c-e] It is possible that the imine nitrogen dissociates from the rhodium centre, as has been seen before through in situ ^{1}HNMR studies,[34f].This would give way for coordination of the olefinic substrate, in a Rh(III)-catalysed hydroformylation pathway (**Scheme 6**).



Scheme 6. Rearrangement that results in formation of a Rh(III) species potentially the active catalyst.

Scope of catalyst precursor C1 in hydroformylation of various olefins

Since the optimum hydroformylation reaction conditions have been established, the scope of **C1** in the hydroformylation of longer chain olefins (C_{10}-C_{12}), methyl/ethyl acrylates and styrene was investigated. Reaction mixtures were analysed using ^{1}H NMR spectroscopy.

Long chain olefins are known to have poor solubility in the aqueous layer which would ultimately affect catalyst contact with organic substrate. However, it has been reported in the literature that conversions observed may be attributed to enriched concentration of the Rh catalyst in the interfacial layer and possible high mobility of substrate between the organic and interfacial layer.[35] From the results summarised in Table 7, the catalyst precursor **C1** gives conversions of 1-decene, 1-undecene and 1-dodecene of >99%.

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Table 7. Hydroformylation of various substrates using C1 as catalyst precursor.

Entry	Substrate	[b]Conv. (%)	Aldehydes (%)			*Iso*-octenes (%)	*n:iso*	TON
			Total	linear	branched			
1	1-Decene	>99	100	30	70	-	0.42	2220
2	1-Undecene	>99	71	32	68	29	0.47	2181
3	1-Dodecene	>99	81	36	64	19	0.57	2200
4	Methyl acrylate	23	100	-	100	-	-	510
5	Ethyl acrylate	35	100	-	100	-	-	777
6	Styrene	9	100	40	60	-	0.67	200

Conditions: Reactions carried out in toluene (5 mL) and distilled water (5 mL) with **C1**-**C3**, (Catalyst loading (1.29 x 10-3 g 2.87 x 10-3 mmol) separately. Substrate used was 1-octene (0.721 g, 6.37 mmol) and n-decane as an internal (0.180 g, 1.26 mmol) over 8 hours. The reactor was flushed with nitrogen thrice, followed by flushing twice with syngas (CO:H2 = 1:1). Average error estimates: ± 0.22 (decene), ± 0.30 (undecene), ± 0.19 (docecene), ± 0.34 (methyl acrylate), ± 0.11 (ethyl acrylate), ± 0.36 (styrene). TON = (mmol of aldehydes/mmol of Rh) and is based on total aldehydes. [b]Conv. = conversion.

The chemoselectivity for aldehydes was >70% with a mixture of linear and branched aldehydes observed. This is similar to what was observed when 1-octene was used as the substrate using catalysts **C1**-**C3**. In the case of C_{10}-C_{12} more branched aldehydes are observed which can be attributed to greater isomerisation in the longer chain substrates before hydroformylation occurs. Lower conversion of 23% and 35% were observed when methyl acrylate and ethyl acrylate were employed as substrates respectively. However, the systems displayed excellent aldehyde chemoselectivity and this could largely be due to the fact isomerization is not possible with the two substrates. Lower TONs of 510 and 777 h^{-1} for methyl acrylate and ethyl acrylate were observed respectively. It is expected that the conversion of 1-dodecene (C_{12}) be lower than that of 1-undecene (C_{11}), however we notice the opposite in this catalytic system with conversion of 1-dodecene being 10% higher than that observed for 1-undecene. However, when the TONs are

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considered the catalyst seems to maintain more or less similar activity. The 10% difference is not a significant difference.

The hydroformylation of styrene is an important process that give access to both linear and branched aldehydes that find use in the production of anti-inflammatory drugs, detergents andplasticizer industries.[36] However, the hydroformylation of styrene usually favours the formation of the branched aldehyde product. This is largely due to the formation of a very stable benzylic rhodium species due to the η2 electron donor emanating from the aromatic system thats induces this regioselectivity.[36] The same phenomenon was observed when **C1** was employed with 60 % branched aldehydes being formed from the aqueous biphasic hydroformylation of styrene. A very poor conversion of only 9% was recorded with 100% aldehyde formation. Styrene also showed very suppressed conversions to the desired products. This could firstly due to the biphasic nature of the catalytic system that hinders maximum contact between the catalyst and substrate. Secondly, our catalysts are clearly not very active as observed by the suppressed results.

Conclusions

Water-soluble N^O complexes **C1-C3** were prepared and characterised and further evaluated as isomerization-hydroformylation catalyst precursors.

Optimum conditions were realised at 85 °C and 40 syngas pressure. The three catalysts displayed excellent substrate conversion of >98% and 100% aldehyde chemoselectivity, interestingly, good selectivity for branched aldehydes was observed and this indicates that isomerization is favoured prior to hydroformylation. Further studies have shown that the catalysts are only not effective in thermodynamically favoured isomerization (isomerization of 1-octene to 2- and 3-octenes) but also promotes contra-thermodynamic isomerization (2-octene to 1-octene). The later is a rare phenomenon which means that these catalytic systems can be further developed for upgrading internal olefins (such as in fatty acids) into high value terminal olefins.

The catalyst precursors with additional water-solubilising groups (**C1** and **C2**) were more active for hydroformylation displaying turnover numbers (TON) of 2208 and 2318, and this may be as a result of better solubility enhancing the activity as compared to **C3**. The aqueous biphasic

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approach to separation (of the products-catalyst solution) was demonstrated for the salicyldamine-based catalysts, since these were successfully separated and recycled for up to three times without any significant loss in catalytic activity and selectivity. The efficacy of **C1** was further evaluated in the aqueous biphasic isomerization-hydroformylation of 1-decene, 1-undecene and 1-dodecene. The catalyst proved to be versatile and excellent substrate conversions with the long chain olefins while lower conversions were recorded with acrylates and styrene. TONs in the range 2100-2300 were observed with the long chain olefins which is very similar to what is observed when 1-octene is used as the substrate. Furthermore, mercury poisoning studies using 1-octene as a substrate confirmed that the catalysis was due to molecular homogenous catalysts, more specifically potentially a Rh(III) hydride catalytically active species as obtained from preliminary computations.

Experimental

Materials and methods

All compounds were prepared using standard Schlenk and vacuum line techniques. Solvents and reagents were purchased from Sigma-Aldrich and were of full analytical grade and were used as received. These reagents include 4-aminobenzoic acid, 4-formyl-3-hydroxy benzoic acid, aniline, salicylaldehyde, 1,5-cyclooctadiene. Sodium 3-(((4-carboxyphenyl) imino) methyl) – 4 hydroxybenzene sulfonate), 4-((2-hydroxybenzylidene) amino) benzoic acid and (4-[(2-thinylmethylene) amino] benzoic acid) were synthesised according to literature. [24-25] $RhCl_3$ was purchased from Heraeus South Africa Pty Ltd. $[RhCl(COD)]_2$ was synthesised following a literature protocol.[26]

Nuclear Magnetic Resonance (^{1}H NMR, ^{13}C{^{1}H} NMR) spectra were recorded on a Bruker Ultrashield 400 (^{1}H NMR 400.17 MHz and ^{13}C{^{1}H} 100.62 MHz) in DMSO-d6 at ambient temperatures while the coupling constants were calculated in Hertz (Hz). The chemical shifts were reported in parts per million (ppm) and relative to tetramethylisane (δ 0.00) as an internal standard. FT-IR spectra were recorded using a Perkin Elmer FT-IR Spectrum BX II fitted with an ATR probe. Elemental analyses were performed on a Thermo Scientific FLASH 2000 CHNS-O analyser. The HR-MS (ESI) spectra were recorded on Walters Synapt G2 Spectrometer. A Gallenkamp digital melting point apparatus was used to determine the melting point. Hydroformylation samples were analysed on a Scion 456-GC with 30 m x 0.25 mm

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cyanopropylphenylmethylpolysiloxane phase column. ICP-MS experiments were conducted on a Perkin Elmer PESCIEX ELAN 6100.

Crystal data was collected on a Bruker APEXII diffractometer with Mo Kα (λ = 0.71073 Å) radiation (Cu Kα (λ = 1.54178 Å) used for 1) and diffractometer to crystal distance of 4.00 cm. The initial cell matrix was obtained from three series of scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about with an exposure time of 10 s per frame. The data were collected using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.75 Å. Data were harvested by collecting 2982 frames at intervals of 0.5º scans in ω and φ with exposure times of 10 s per frame.[37] A successful solution by the direct methods of SHELXS 2013 provided all non-hydrogen atoms from the E-map. All nonhydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms (except the ones participating in hydrogen bonding interactions) were included in the structure factor calculation at idealized positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients.[38] The systematic absences in the diffraction data were uniquely consistent for the space group P21/n that yielded chemically reasonable and computationally stable results of refinement.[39-43] CCDC 1896188 for **C3** contains the supplementary crystallographic data for this paper.

Synthesis of ligands L1 – L3

*Synthesis of **L1***

(40 mg, 0.3 mmol) 4-amino benzoic acid was dissolved in ethanol, (50 mg, 0.3 mmol) 4-formyl-3-hydroxy benzoic acid was added to the reaction vessel and the mixture was heated at 50 ºC for 16 hours. The mixture turned orange within minutes (approximately 5 minutes) of stirring. After 16 hours, a peach precipitate had formed and was isolated by suction filtration then dried using a high vacuum pump for 2 hours.

Yield 0.055 g (64 %). Melting point: 300-304 ºC. ^{1}H NMR (400 MHz, DMSO-d6, 22 ºC) (ppm) = 12.55 (br s, 1H, OH) 9.04 (s, 1H, H_{imine}), 8.02 (d, $^{3}J_{H-H}$ = 8.8 Hz, 2H, H_{Ar}), 7.85 (d, $^{3}J_{H-H}$ = 8 Hz, 1H, H_{Ar}), 7.52 (m, 4H, H_{Ar}). $^{13}C\{^{1}H\}$ NMR (400 MHz, DMSO-d6, 22 ºC) (ppm) = 167.9, 160.9, 153.6, 131.7, 131.2, 128.9, 122.1, 121.0, 120.0, 89.0, 120.2, 118.5, 117.3, 113.0. Elemental analysis: Calculated for $C_{15}H_{11}NO_5$: C 63.16, H 3.89, N 4.91 %. Found: C 62.93, H

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3.93, N 4.80 %. HR-MS (ESI^+): Calculated for $C_{11}H_{11}NO_5$, *m/z* = 285.0637 $[M]^+$, Found:, *m/z* = 286.0256 $[M+H]^+$. FT-IR (ν_{max}/cm^{-1}) (ATR): 1678 (C=N), 1698 (C=O). Solubility: not soluble in DCM, MeOH, EtOH, and H_2O, soluble in H_2O at 65 °C.

*Synthesis of **L2***

Monosodium 5-sulfonatosalicylaldehyde (0.58 g, 0.0026 mol) and 4-aminobenzoic acid (0.36 g, 0.0026 mol) were heated in ethanol at 60 °C for about 15 hours. After 15 hours, a yellow precipitate (**L2**) formed which was then isolated by suction filtration and washed with portions of cold ethanol (2 x 30 ml). Following the washing of **L2**, was dried under vacuum for 3 hours.

Yield 0.63 g (71%). Melting point: decomposes without melting, onset occurs at 195 °C. ^1H NMR (400 MHz, DMSO-d6, 22 °C): 9.00 (s, 1H, H_{Imine}), 7.98 (m, 3H, H_{Ar}), 7.65 (m, 1H, H_{Ar}), 7.45 (d, $^3J_{H-H}$ = 8 Hz, 2H, H_{Ar}), 6.94 (d, $^3J_{H-H}$ = 8 Hz, 1H, H_{Ar}). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d6, 22 °C) (ppm) = 167.4, 164.4, 160.2, 153.1, 152.0, 140.0, 130.6, 121.5, 118.0, 116.8, 115.8, 112.5. Elemental analysis calculated for $C_{14}H_{10}NNaO_6S$: C 48.98, H 2.94, N 4.08 %. Found: C 48.73, H 2.97, N 4.63 %. HR-MS (ESI^-): calculated for $C_{14}H_{10}NNaO_6S$, *m/z* = 343.0253 $[M]^+$, found: *m/z* =317.1280 $[M\text{-}Na\text{-}2H]^+$. FT-IR ($\nu_{max}/cm^{-1}$, ATR): 1618 cm^{-1}(C=N), 1700 (C=O). Solubility: Not soluble in: toluene, MeOH, EtOH, DCM, EtOAc. Soluble in H_2O (65°C).

*Synthesis of **L3***

4-Aminobenzoic acid (1.37 g, 10.0 mmol) was dissolved in 50.0 mL EtOH in a 100 mL round bottom flask. Then 2 drops of glacial acetic acid were added followed by salicylaldehyde (1.06 mL, 10.0 mmol), and the reaction solution was heated at 50 °C for 3 hours during which time an orange precipitate formed. The reaction mixture was filtered by suction to isolate the orange precipitate from the solvent. The prodcut was washed with EtOH (2 x 30 mL) then dried under vacuum for 18 hours.

Yield: 2.16 g (89%). Melting point: 265-268 °C. ^1H NMR (400 MHz, DMSO-d6, 22 °C) (ppm) = 12.95 (br s, 2H, H_{COOH})12.71 (br s, 1H, H_{OH}) 8.98 (s, 1H, H_{imine}), 8.01 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, H_{Ar}), 7.69 (d, $^3J_{H-H}$ = 1.2 Hz, 2H, H_{Ar}), 7.48 (m, 3H, H_{Ar}) 6.98 (m, 2H, H_{Ar}). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d6, 22 °C) (ppm) = 167.8, 161.2, 160.8, 153.6, 136.8, 134.3, 131.2, 129.3, 121.9, 119.9, 117.7, 113.0. Elemental analysis calculated for $C_{14}H_{11}NO_3$: C 69.70, H 4.60 N 5.81 %. Found: C 70.39 H 4.71, N 5.79 %. HR-MS (ESI^-): Calculated for $C_{14}H_{11}NO_3$: *m/z* = 241.0673

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$[M]^+$, found: *m/z* = 242.0809 $[M+H]^+$. FT-IR (ν_{max}/cm^{-1}, ATR): 1677 (C=N), 1700 (C=O). Solubility: Sparingly soluble in toluene, MeOH, EtOH, completely soluble in DCM and EtOAc. Soluble in H_2O (65°C).

Synthesis of complexes C1-C3

*Synthesis of [Rh(**L1**)(COD)],* ***C1***

L1 (25 mg, 0.1 mmol) was dissolved in an EtOH:H_2O mixture (50:50), (20 mL). 0.1 M KOH(*aq*) (1.00 ml, 0.1 mmol) was added to the solution and it was left to stir at room temperature for 30 minutes. $[RhCl(COD)]_2$ (25 mg, 0.05 mmol) was then added to the reaction solution and this was stirred at room temperature for a further 3 hours. An orange precipitate formed which was then isolated by suction filtration, washed with EtOH (2 x 20 mL) and dried under vacuum for 4 hours.

Yield 0.026 g, (100%). Melting point: 340-344 °C. ^1H NMR (400 MHz, DMSO-d6, 22 °C) (ppm) = 8.35 (s, 1H, H_{imine}), 7.96 (d, ^3J = 8Hz, 2H, H_{Ar}), 7.54 (d, ^3J = 8 Hz, 1H, H_{Ar}), 7.25 (d, ^3J = 8 Hz, 2H, H_{Ar}), 7.21 (s, 1H, H_{Ar}), 7.04 (d, ^3J = 8 Hz, 1H, H_{Ar}), 4.38 (m, 4H, H_{COD}), 2.29 (m, 4H, H_{COD}), 1.71 (m, 4H, H_{COD}). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d6, 22 °C) (ppm) = 167.9, 160.9, 153.6, 131.7, 131.2, 129.8, 128.9, 122.1, 120.2, 118.5, 117.3, 115.4, 113.0, 78.3, 30.5. Elemental analysis: Calculated for $C_{23}H_{22}NO_5Rh$: C 55.77, H 4.48, N 2.83 %. Found: C 55.44, H 4.79, N 2.77 %. HR-MS (ESI^+): Calculated for $C_{23}H_{22}NO_5Rh$, *m/z* = 495.0612 $[M]^+$, found *m/z* = 497.9933 $[M+3H]^+$, *m/z* = 388.9996 $[M-(COD)]^+$. FT-IR (ν_{max}/cm^{-1}, ATR): 1584 (C=N). Solubility: Soluble in THF and H_2O (65°C), insoluble in MeOH, EtOH, DCM.

*Synthesis of [Rh(**L2**)(COD)]*, ***C2***

L2 (0.18 g, 0.5 mmol) was dissolved in an EtOH-H_2O mixture (50:50), (20 mL). 0.1 M KOH(*aq*) (5.00 ml, 0.5 mmol) was added to the solution and this was left to stir at room temperature for 30 minutes. $[RhCl(COD)]_2$ (0.12 g, 0.25 mmol) was then added to the solution and this was stirred at room temperature for a further 3 hours. A yellow precipitate formed which was isolated by suction, washed with EtOH (2 x 20 mL) and dried under vacuum for 5 hours.

Yield 011 g (78%). Melting point: decomp without melting, onset at 280 °C. ^1H NMR (400 MHz, DMSO-d6, 22 °C) (ppm) = 9.03 (s, 1H, H_{Imine}), 8.20 (s, 1H, H_{Ar}), 7.90 (d, ^3J = 8 Hz, 2H, H_{Ar}), 7.54 (d, ^3J = 4 Hz, 1H, H_g), 7.09 (d, ^3J = 8 Hz, 1H, H_{Ar}), 6.63 (d, ^3J = 8 Hz, 1H, H_{Ar}), 4.34

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(m, 4H, H_{COD}), 2.29 (m, 4H, H_{COD}), 1.73 (m, 4H, H_{COD}). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d6, 22 ^oC) (ppm)= 167.4, 166.8, 164.4, 160.2, 153.1, 152.0, 140.0, 131.1, 130.6, 121.5, 118.0, 116.8, 81.6, 29.9. Elemental analysis: Calculated for $C_{22}H_{21}O_6NRhNa$: C 48.98, H 2.94, N 4.08 %. Found: C 48.77, H 2.23, N 4.63 %. HR-MS (ESI^+): Calculated for $C_{22}H_{21}O_6NRhNa$ *m/z* = 553.3786 $[M]^+$, found *m/z* = 555.0132 $[M+2H]^+$. FT-IR (ν_{max}/cm^{-1}, ATR): 1590s (C=N), 1702 (C=O. Solubility: Soluble in H_2O, insoluble in toluene, DCM, EtOH, MeOH, EtOAc.

*Synthesis of [Rh(**L3**)(COD)]*, ***C3***

L3 (25 mg, 0.1 mmol) was dissolved in an EtOH-H_2O mixture (50:50), (20 mL). 0.1 M KOH(*aq*) (1.00 ml, 0.1 mmol) to the solution and this was left to stir at room temperature for 30 minutes. $[RhCl(COD)]_2$ (25 mg, 0.05 mmol) was added to the reaction solution and this was stirred at room temperature for a further 3 hours. A yellow precipitate formed which was isolated by suction filtration, washed with EtOH (2 x 20 mL) and dried under vacuum pump for 5 hours. Yield 0.026 g (85%). Melting Point: 298-301 °C. ^1H NMR (400 MHz, DMSO-d6, 22 ^oC) (ppm) 8.22 (s, 1H, H_{Imine}), 7.95 (d, ^3J = 8 Hz, 2H, H_{Ar}), 7.43 (d, ^3J = 8 Hz, 1H, H_{Ar}), 7.33 (t, ^3J = 4 Hz, 1H, H_{Ar}) 7.20 (d, ^3J = 8 Hz, 2H, H_{Ar}), 6.72 (d, ^3J = 8 Hz, 1H, H_{Ar}), 6.55 (t, ^3J = 8 Hz, 1H, H_{Ar}), 4.43 (s, 4H, H_{COD}), 2.28 (s, 4H, H_{COD}), 1.74 (m, 4H, H_{COD}). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d6, 22 ^oC) (ppm) = 166.0, 165.7, 155.4, 136.5, 135.7, 130.2, 129,3, 125,5, 123.9, 121.3, 118.5, 114.8, 79.0, 30,9. Elemental analysis: Calculated for $C_{22}H_{22}O_3NRh$: C 58.55, H 4.91, N 3.10 %. Found: C 57.4, H 4.94, N 3.15 %. HR-MS (ESI^+): Calculated for $C_{22}H_{22}O_3NRh$ *m/z* = 451.3209 $[M]^+$, found *m/z* = 453.2105 $[M+2H]^+$, *m/z* = 348.9327 $[M-(COD)+3H]^+$. FT-IR (ν_{max}/cm^{-1}, ATR): 1564s (C=N), 1698 (C=O). Solubility: Soluble in H_2O (65 ^oC) DCM, EtOAc. Sparingly soluble in: toluene and MeOH.

General procedure for the catalytic hydroformylation experiments

Hydroformylation reactions were done in a 50.0 mL stainless steel pipe reactor. The reactor was charged with water (5 mL) containing the rhodium(I) catalyst precursor (2.87 x 10^{-3} mmol) and with the organic solvent toluene (5.00 mL) containing the substrate 1-octene (6.37 mmol) and the internal standard *n*-decane (1.26 mmol). N_2 gas was used to flush the reactor three times followed 1:1 syngas (30-50 barss). This was followed by heating the reactor to the desired temperatures, 75-95 °C and stirring. The reactions were performed for 8 h with the samples

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being taken at an initial time = 0 h and final time = 8 h and these were analysed by GC. All products were confirmed with respect to authentic *iso*-octenes and aldehydes.

In the recycling experiments, upon reaction completion, the organic layer was separated by decantation and a fresh organic layer containing the substrate and the internal standard was introduced for the catalyst recycling experiments. All reactions were conducted in duplicates and the results were reported as averages for the identical experiments.

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Conflict of interest

There are no conflicts to declare.

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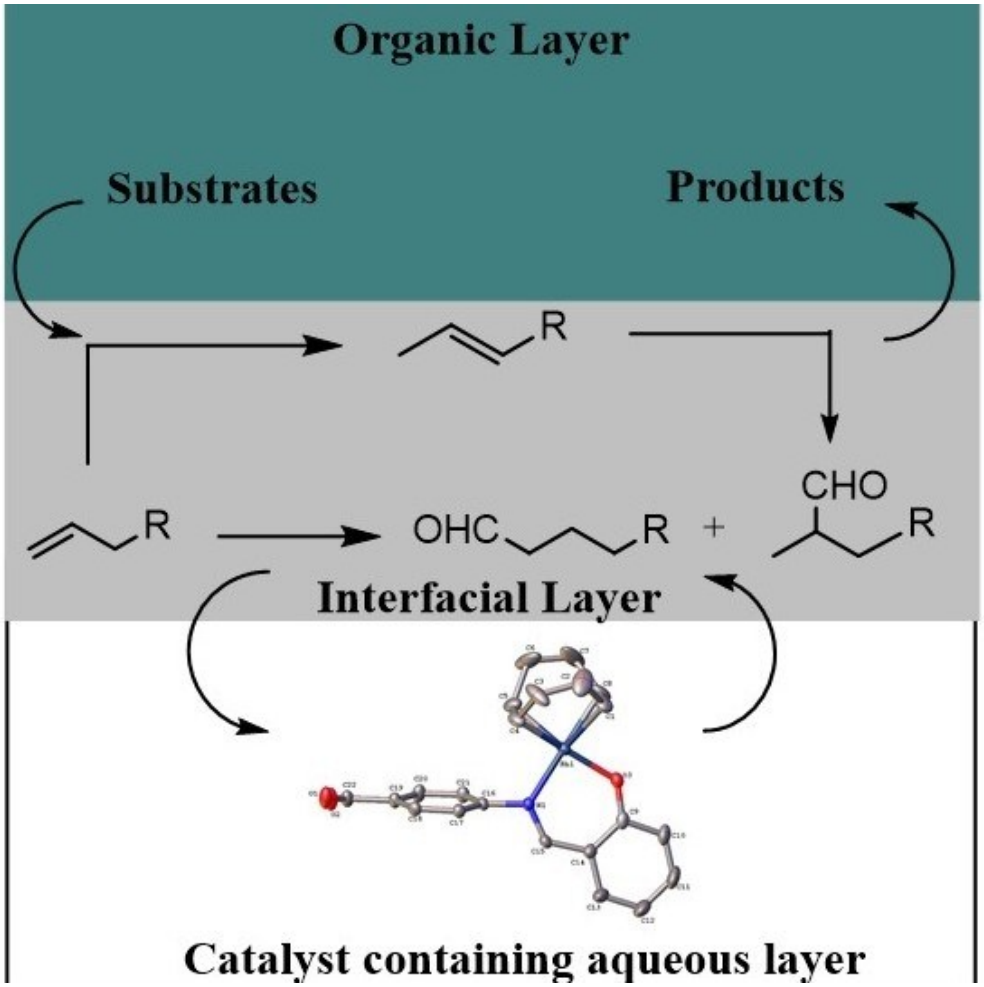

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