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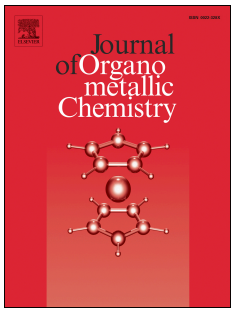

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Synthesis of Rh(I) alkylated-PTA complexes as catalyst precursors in the aqueous-biphasic hydroformylation of 1-octene

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Abstract

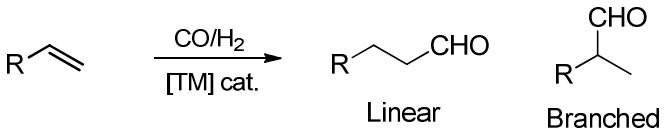
A series of mono- and multivalent phosphorus-based ligands were synthesised by the lower-rim benzylation of the water-soluble ligand, 1,3,5-triaza-7-phosphaadamantane (PTA). These ligands were used to prepare mono-, bi- and trinuclear Rh(I) complexes whose catalytic activity, product selectivity and recyclability were evaluated in the aqueous biphasic hydroformylation of 1-octene.

Introduction

Catalysis plays a very important role in the chemical industry and aids in the production of over 90% of all industrial chemicals produced [1,2]. Using a catalyst lowers the reaction's energy requirements, increases product selectivity and often reduces the use of processing and separating agents [3–5]. The use of transition metals as catalysts has been vastly explored [6]. Homogeneous catalysis has significant advantages over heterogeneous catalysis because it displays greater activity and selectivity [7]. The major disadvantage with homogeneous catalysis is separating the catalyst from the products obtained [8]. A number of strategies [9–12] have been employed to combat the separation challenge, including immobilising the catalyst using biphasic media [13]. In recent years, there has been a considerable interest in the synthesis of water-soluble catalysts for use in a number of reactions such as hydrogenation [14,15], carbonylation [16], alkene metathesis [17,18] and hydroformylation [19,20].

The hydroformylation of olefins (Scheme 1) has grown to be an important industrial process since the obtained aldehydes can be used to manufacture plasticisers, surfactants and

detergents, chemical intermediates, solvents and lubricants [21]. The hydroformylation reaction is an extensively studied process and much attention has been given to the design and synthesis of new metal complexes that exhibit improved catalytic activity, greater product selectivity and can easily be reused.



Scheme 1: Illustration of the hydroformylation reaction.

New metal complexes as catalysts for hydroformylation reactions continue to be studied due to the need for simple and effective catalysts to facilitate complex catalytic reactions such as in the aqueous biphasic hydroformylation of olefins. Aqueous biphasic hydroformylation (Figure 1) combines the advantages of homogeneous and heterogeneous catalyses and uses water as the second immiscible phase solvent. Innovative work into aqueous biphasic catalysis can be traced back to the Ruhrchemie/Rhône-Poulenc (RCH/RP) industrial process and several other academic reactions that make use of a highly water-soluble rhodium complexes as catalysts for the hydroformylation of propene [22]. The use of water is in line with Green Chemistry Principles due to water being eco-friendly, user-friendly, non-toxic, abundant (hence relatively cheap) and non-flammable. Moreover, water is immiscible with most organic solvents, addressing the challenge of catalyst recovery [8].

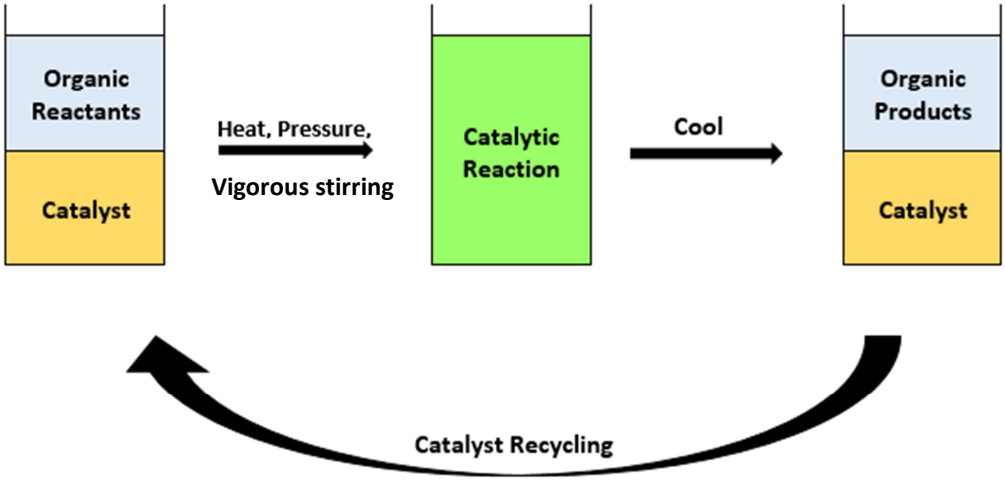


Figure 1: Illustration of aqueous biphasic hydroformylation.

To obtain water-soluble metal complexes, hydrophilic ligands are usually introduced into the coordination sphere of the metal centre [23]. Water-soluble phosphines are the most widely used [24], because they can be modified using a variety of organic substituents, which in-turn affects the electronic and steric characteristics of the catalyst [25]. 1,3,5-Triaza-7-phopsphaadamantane (PTA) is a water-soluble phosphine and its metal complexes have been studied and found to be useful in catalysing many chemical reactions, including the hydrogenation of olefinic and oxo acids [26], isomerisation and condensation of allyl alcohol [27] and the reduction of aldehydes [28,29].

A more recent approach to improving the catalyst's activity has been to increase the number of metal centres. This motivation comes from nature's highly selective metalloenzymes. Having more than one metal centre introduces cooperative interactions that may exist between proximate metal centres, enhancing catalytic activity compared to the mononuclear analogues [30]. Park and Hong suggested that the ideal distance for cooperativity between two metal centres is within 3.5 - 6 Å, with the exception of those which exhibit a direct metal-metal bond. Thus, if the metals are an appropriate distance from each other, higher reactivity and selectivity can be achieved as compared to when using the monometallic complexes [31].

Coordinating highly water-soluble ligands, such as PTA, to the rhodium metal centre and increasing the number of metal centres (rhodium atoms) per complex may further improve catalytic rates, product selectivity and recovery of the catalyst in hydroformylation reactions.

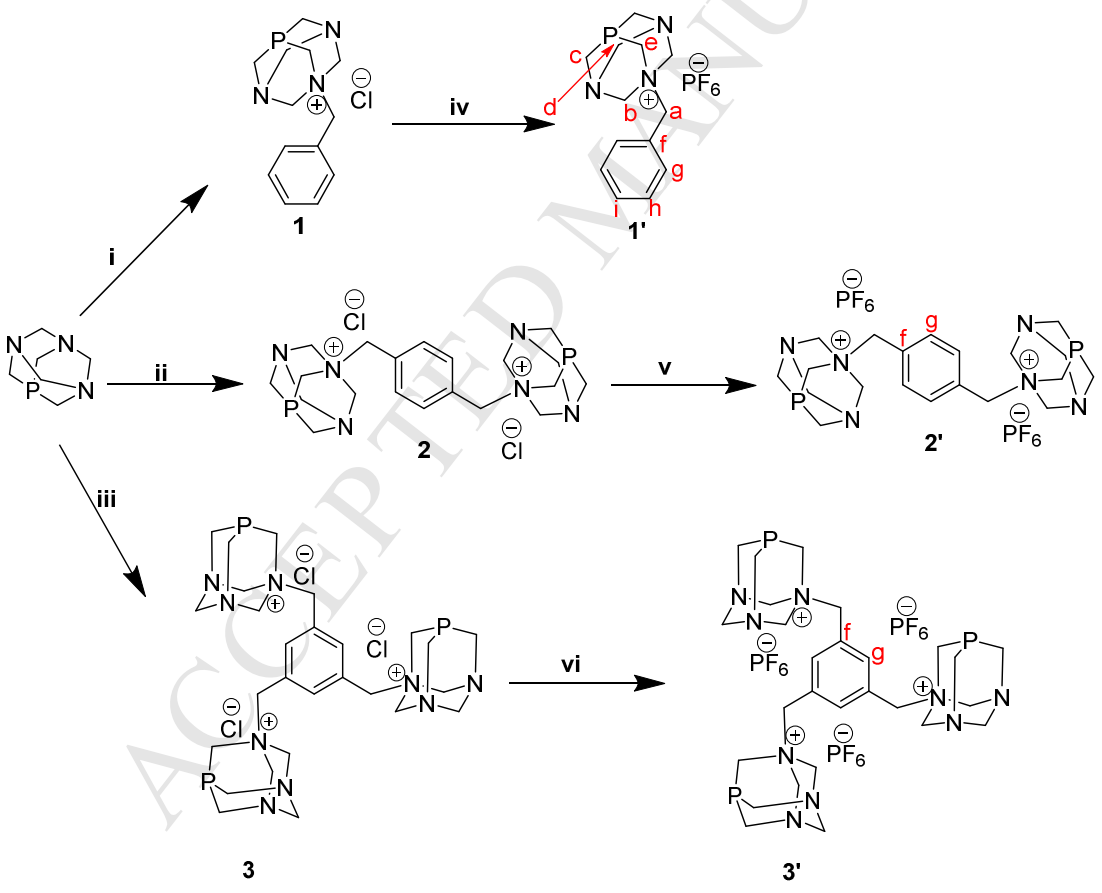
In this work, the syntheses and characterisation of a series of PTA ligands is reported. The mono-, bi- and trimeric phosphine-based ligands were synthesised by the alkylation of PTA. These ligands were then reacted with the appropriate equivalent of the rhodium precursor $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) to afford the corresponding mono-, bi- and trinuclear Rh(I)-PTA complexes. The resulting complexes were then reacted with carbon monoxide gas to yield the dicarbonyl analogues of the Rh(I)-PTA complexes. All complexes

were then evaluated as catalyst precursors in aqueous biphasic hydroformylation of 1-octene.

Results and discussion

*Synthesis and characterisation of ligands **1 – 3** and **1' – 3'***

The benzylated PTA derivatives were prepared as previously described in literature [32–34]. The benzylic halides (benzyl chloride, 1,4-bis(chloromethyl)benzene, and 1,3,5-tris(chloromethyl)benzene) were reacted with appropriate equivalents of PTA to afford ligands **1**, **2**, and **3** respectively (Scheme 2). Ligands **1** and **2** were isolated as white solids and ligand **3** as a beige solid in moderate to good yields (38 – 97 %) and were all water-soluble. The signals in the ^{1}H NMR correlate with those reported in literature [32–34].



i) Benzyl Chloride, MeOH, 70 °C, 2 hrs
ii) 1,4-bis(chloromethyl)benzene, Acetone, 60 °C, 2 hrs
iii) 1,3,5-tris(chloromethyl)benzene, Acetone, 60 °C, 18 hrs
iv) NH_4PF_6 , EtOH, r.t., 20 hrs
v) NH_4PF_6 , EtOH, r.t., 72 hrs
vi) NH_4PF_6 , EtOH, r.t., 96 hrs

Scheme 2: Syntheses of the monomeric, dimeric and trimeric ligands.

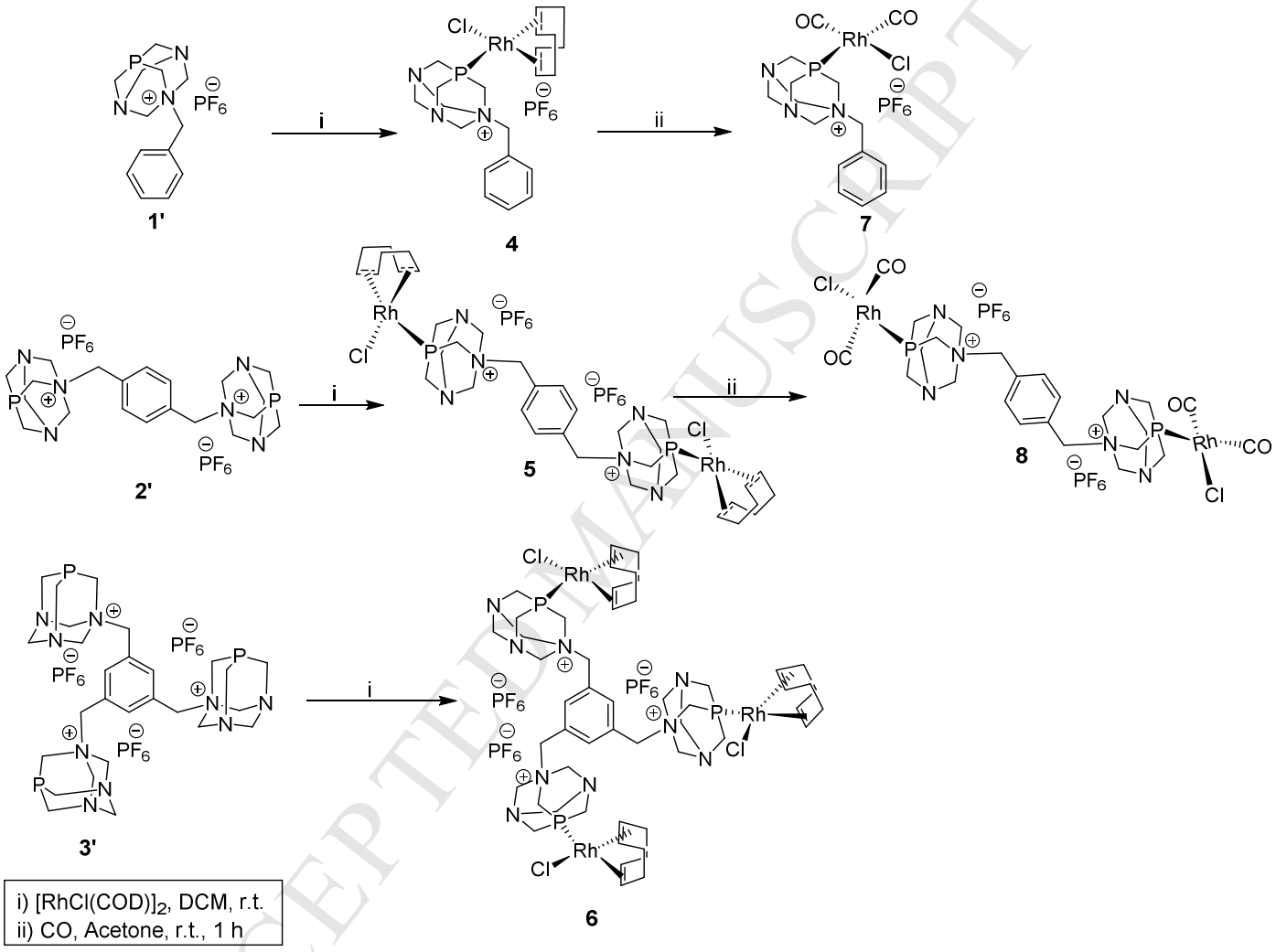
Complexation reactions were attempted by reacting ligands **1**, **2** and **3** with $[RhCl(COD)]_2$ and the resulting products were found to be unstable. A counterion exchange was then performed, replacing the chlorido anions with the much larger hexaflurophosphate anions. Ligands **1'**, **2'** and **3'** were prepared by reacting each of ligands **1** – **3** with the appropriate equivalent of NH_4PF_6 in ethanol (Scheme 2) and were obtained as white solids in moderate to good yields (51 – 94 %). The proton signals observed in the ^1H NMR spectra of ligands **1' – 3'** show a similar splitting pattern as in the ^1H NMR spectra of ligands **1 – 3**. In addition, a slight upfield shift of the PTA proton signals when compared to the ^1H NMR spectra of ligands **1 – 3** was observed, confirming successful anion exchange. Furthermore, the $^{31}P\{^1H\}$ NMR spectra also confirms successful anion exchange, as two phosphorus entities are observed for each of ligands **1' – 3'** (as opposed to a single signal for each of ligands **1 – 3**), the signal corresponding to the PTA phosphorus entity, which shifts upfield, and a septet for the PF_6^- phosphorus entity.

*Synthesis and characterisation of the Rh(I)-PTA complexes (**4 – 6**)*

The mononuclear (**4**), binuclear (**5**) and trinuclear (**6**) complexes were prepared in order to investigate the effect of increasing the number of metal centres on the activity and selectivity in the hydroformylation of 1-octene. Ligands **1'**, **2'** and **3'** were each reacted with $[RhCl(COD)]_2$ to afford complexes **4**, **5** and **6** respectively (Scheme 3). The complexes were obtained as yellow solids in good yields (61 – 94 %). The metal complexes are sparingly soluble in water at room temperature, largely due to the highly hydrophobic PF_6^- counterions. Solubility studies conducted at 40 °C in water gave an average solubility of 2 mg/mL for complexes **4 – 6**.

Coordination of the ligands to the metal centre is confirmed by three new signals in the ^1H NMR spectrum of each of complexes **4**, **5** and **6** accounting for the COD protons. Coordination of the ligands *via* the phosphorus atom is further corroborated by the $^{31}P\{^1H\}$ NMR spectra. Each of the $^{31}P\{^1H\}$ NMR spectra of complexes **4**, **5** and **6** show doublets at δ = -32.67 with coupling constant $J_{Rh\text{-}P}$ = 136.0 Hz, at δ -32.17 with coupling constant $J_{Rh\text{-}P}$ = 157.9 Hz and δ = -32.38 with coupling constant $J_{Rh\text{-}P}$ = 145.5 Hz respectively. The

ESI-MS(+) spectrum for complex **4** shows a base peak at *m*/*z* = 264.1263 corresponding to adduct $[M–PF_6+Na]^{2+}$. A base peak is observed at *m*/*z* = 312.9192 for complex **5** corresponding to $[M–2PF_6+Na]^{3+}$ and the mass spectrum for complex **6** shows a base peak at *m*/*z* = 476.9400 corresponding to $[M–3PF_6]^{3+}$.



Scheme 3: Synthesis of the Rh(I)-PTA catalyst precursors (**4 – 6**) and their carbonyl analogues (**7 – 8**).

The carbonyl (CO) analogues **7** and **8** were synthesised following a published literature method with minor modifications (Scheme 3) [35–37]. The rationale for the preparation of these complexes is based on different electronic and steric properties that arise from the COD and CO ligands. CO is a good π-acceptor and hence electron density can be back-donated from the metal centre to the CO ligand, leaving the metal centre electron deficient. Thus, the electron density around the rhodium of the complexes bearing the CO ligands is expected to be less than the electron density around the rhodium of the complexes bearing

the COD ligands. Moreover, CO is a less bulky ligand than the COD ligand and would possibly influence the regioselectivity during the catalytic reactions in a different manner to the COD ligand.

Each of complexes **4** and **5** were reacted with gaseous CO (Scheme 3) to afford complexes **7** and **8** as light orange solids in good to excellent yields (70 – 98 %). Despite several attempts under varying conditions, including increasing the temperature and CO pressure, the CO analogue of the trinuclear complex **6** could not be successfully isolated. This could be due to the poor solubility of complex **6** in most organic solvents.

The successful synthesis of complex **7** was confirmed by the absence of the COD proton signals and the slight upfield shift of the PTA proton signals in the ^{1}H NMR spectrum. The $^{13}C\{^{1}H\}$ NMR spectrum of **7** further confirms the formation of this complex. A signal is observed at δ = 192.08 assigned to the CO ligands. The signal corresponding to the PTA phosphorus entity in $^{31}P\{^{1}H\}$ NMR also shows an upfield shift indicating successful substitution of the COD ligand for the CO ligands.

Infrared (IR) spectroscopy further corroborates the substitution of the COD ligand with the CO ligands. The presence of two ν(C≡O) absorption bands at 2048 and 1996 cm^{-1} suggest that the two CO ligands are in different chemical environments. The two CO ligands are *cis* to each other in solid state, i.e. one is *trans* to the chlorido ligand and the other is *trans* to the PTA ligand. Similar shifts in the ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra and similar IR patterns were also observed for complex **8**. The ESI-MS(+) spectra show a base peaks at *m*/*z* 248.1313 corresponding to $[M–PF_6+Na]^{2+}$ (for complex **7**) and at *m*/*z* 268.1862 $[M–2PF_6+H]^{3+}$ for complex **8**.

Aqueous biphasic hydroformylation of 1-octene

The mononuclear (**4**), 1,4-dinuclear (**5**) and the trinuclear (**6**) complexes were utilised for the initial catalytic studies in order to determine optimal conditions for the aqueous biphasic hydroformylation of 1-octene. These experiments were performed at temperatures of 50, 75 and 95 °C and 20, 30 and 40 bars of syngas pressure ($CO:H_2$ = 1:1) in toluene (5 mL) and water (5 mL). All catalytic reactions were carried out in duplicate for 8 hours. The catalyst

loading was maintained at $2.87x10^{-4}$ mol% with respect to the rhodium metal centre (Rh:substrate = 1:2500) for each catalyst precursor. Complexes **7** and **8** were then evaluated as catalyst precursors in the hydroformylation of 1-octene at the optimal conditions determined.

Table 1: Hydroformylation results of 1-octene over 8 hours.

Entry	Catalyst	Pressure (bar)	Temperature (°C)	Conversion (%)[a]	Aldehydes (%)[b]			Iso-octenes (%)[b]	*n*:iso[c]	TOF (h^{-1})[d]
					Total	linear	branched			
1	**4**	20	50	10	67	68	32	33	2.1	22
2		20	75	95	46	60	40	54	2.6	102
3		20	95	98	42	55	45	58	1.2	130
4		30	50	10	77	65	35	23	1.9	24
5		30	75	98	69	59	41	31	1.4	212
6		30	95	96	45	52	48	55	1.9	136
7		40	50	17	80	64	36	20	1.8	41
8		40	75	99	93	52	48	7	1.1	288
9		40	95	99	94	46	54	6	0.8	292
10	**5**	20	50	16	63	68	32	37	2.1	31
11		20	75	97	55	63	37	45	2.1	125
12		20	95	99	50	41	59	50	0.7	195
13		30	50	22	78	68	32	22	2.1	44
14		30	75	98	74	59	41	26	1.4	227
15		30	95	99	63	43	57	37	0.8	241
16		40	50	26	71	62	38	29	1.7	57
17		40	75	98	75	61	39	25	1.6	206
18		40	95	99	80	42	58	20	0.7	247
19	**6**	20	50	48	63	68	32	37	2.1	91
20		20	75	98	61	55	45	39	1.2	187
21		20	95	96	67	40	60	33	0.7	199
22		30	50	50	83	65	35	17	1.9	121
23		30	75	99	79	52	48	21	1.1	255
24		30	95	99	76	42	58	24	0.7	245
25		40	50	51	82	62	38	18	1.7	122
26		40	75	98	91	52	48	9	1.1	278
27		40	95	98	91	44	56	9	0.8	263
28	**7**	40	75	80	74	79	21	26	3.8	223
29	**8**	40	75	86	78	73	27	22	2.5	213

Reactions carried out in toluene (5 mL) and distilled water (5 mL) with 7.18 mmol of 1-octene and 2.87×10^{-3}, 1.44×10^{-3} and 9.57×10^{-4} mmol of each of catalyst precursors **4**, **5** and **6** respectively varying the temperature (50, 75 and 95 °C) and pressure (20, 30 and 40 bar) of syngas ($CO:H_2$ = 1:1). GC conversions were obtained using *n*-decane as an internal standard in relation to authentic standard *iso*-octenes and aldehydes. TOF = (mol product/mol catalyst)h^{-1} and is based on total aldehydes. Average error estimates: [a]±2.1, [b]±1.5, [c]±0.1 % and [d]±4.2 %

Effect of temperature

The reactions were carried out at 50, 75 and 95 °C. At 50 °C, all three catalyst precursors exhibit low conversion, with the highest conversion being 51 % (with complex **6**) at 30 bar.

In general, the conversion of 1-octene largely increases (>90 %) when the reactions are carried out at 75 and 95 °C. For **5** and **6**, a temperature of 75 °C favours linear aldehydes whereas at 95 °C branched aldehydes are favoured. When catalyst precursor **4** is used, linear aldehydes are favoured both at 75 and 95 °C. Thus, when using **5** and **6** as pre-catalysts for the hydroformylation of 1-octene, the temperature should be selected according to the type of desired aldehyde (linear or branched).

Effect of pressure

Reactions were carried out at 20, 30 and 40 bars. For catalyst precursors **4** and **6** the reactions carried out at 40 bars exhibit higher chemoselectivity (up to 93 % aldehydes with complex **4** at 75 °C) than at 20 and 30 bars. Catalyst precursor **5** exhibits a minimal formation of the hydrogenation product, octane (8 % and 14 % at 75 and 95 °C respectively) at a pressure of 40 bars.

Effect of increasing metal centres

There is no significant difference in hydroformylation results obtained (conversion and selectivity) when using catalyst precursors **4** and **5**. When the catalyst precursor **6** is employed, a significantly higher conversion of 1-octene is observed at 50 °C (up to 51 % at 30 bar) when compared to the very poor conversion seen when using **4** and **5** (highest being 26 % with **5** at 40 bar). This implies that the catalyst **6** exhibits faster rates than the mononuclear (**4**) and binuclear catalysts (**5**).

Optimal conditions

At low temperature (50 °C) the catalyst precursors exhibit poor conversion of 1-octene. The optimal temperature was established to be 75 °C, which favours linear aldehydes over branched aldehydes and the optimal pressure is 40 bar, which in turn exhibits better chemoselectivity towards aldehydes. All three complexes exhibit good catalytic activity at these optimal conditions, with TOF values ranging between 200 and 300 h^{-1}.

*Performance of COD complexes (**4** – **6**) and CO complexes (**7** and **8**) compared*

All complexes exhibit very good to excellent conversion (greater than 80 %). The COD containing catalyst precursors (**4 – 6**) show greater conversion and are generally more active (with TOF values as high as 288 h^{-1}, entry 8) than **7** and **8**, the dicarbonyl analogues. This could be attributed to the difference in electronic properties of the COD and CO ligands. Further studies would have to be conducted in order to determine the mechanism of the catalytic reactions when using catalyst precursors **4 – 8**. This would assist in further explaining the difference in conversion of 1-octene when using the catalyst precursors (**4 – 6**) and the CO pre-catalysts (**7** and **8**).

The chemoselectivity of the catalyst precursors at optimal conditions is displayed graphically in Figure 2. The COD complexes (**4 – 6**) display better chemoselectivity for aldehydes compared to the CO catalysts (**7** and **8**). This is attributed to the COD complexes reaching near quantitative conversion after 8 hours, as a result, most of the iso-octenes that have formed are hydroformylated leading to a decrease in the amount of iso-octenes present and an increase in the amount of total aldehydes produced. No hydrogenation products (alkanes and alcohols) are observed for any of the catalyst precursors.

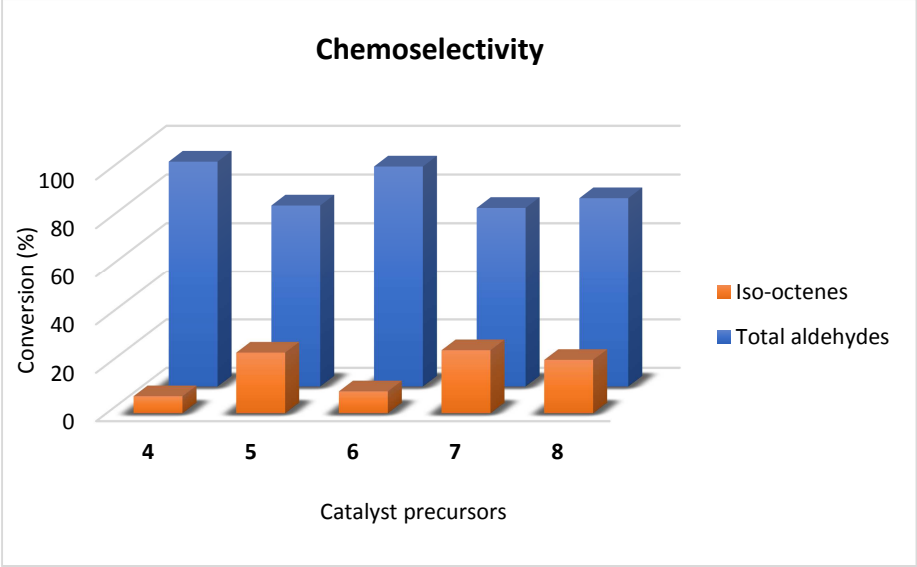


Figure 2: Chemoselectivity of the catalyst precursors studied for the aqueous biphasic hydroformylation of 1-octene.

The CO catalyst precursors (**7** and **8**) display better regioselectivity compared to the COD containing catalyst precursors (**4 – 6**) at optimal conditions (75 °C and 40 bar), as shown by the graph in Figure 3. The *n*:iso ratios of the COD containing catalyst range between 1.1 and 1.6 whilst the *n*:iso ratios of the CO complexes go as high as 3.8 (entry 28). This is consistent with results obtained by Makhubela *et al*. when comparing regioselectivity exhibited by rhodium pre-catalysts that have COD and CO as ligands [38]. This means that the dicarbonyl complexes are more selective for linear aldehydes than the COD complexes, a result that was not expected as the COD ligand is bulkier than the carbonyl ligand and thus catalyst precursors with COD ligands would be expected to exhibit selectivity towards linear aldehydes than the complexes with the CO ligands. This could be due to the fact that with CO ligands the PTA ligand can move freely, as opposed to when a bulky COD ligand is in the vicinity. Such movement may result in desirable steric effects around the rhodium metal centre, therefore favouring linear aldehydes (i.e. high *n*:iso ratios).

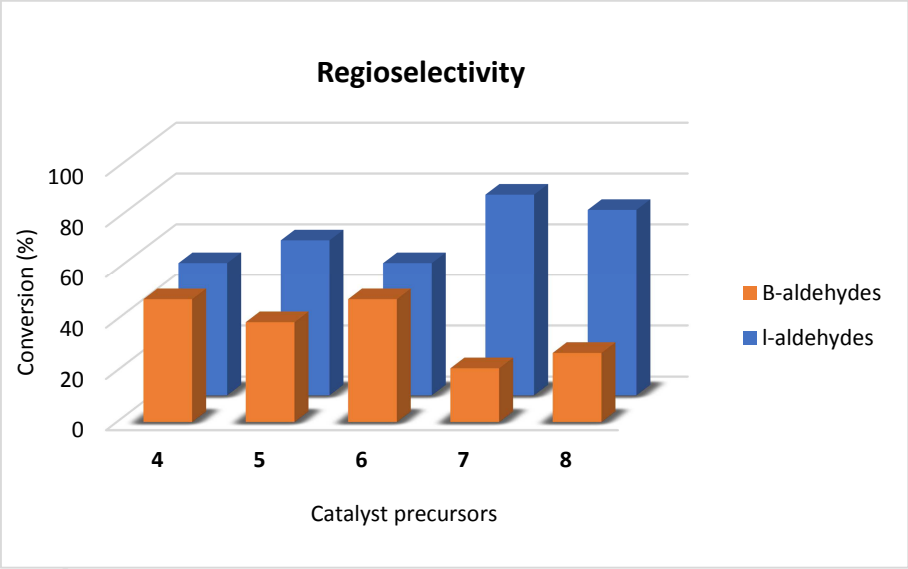


Figure 3: Regioselectivity of the catalyst studied for the aqueous biphasic hydroformylation of 1-octene.

Performance of catalyst precursors over time

No significant difference in the activity and selectivity is observed with an increase in the number of metal centres. This motivated the study of the performance of catalyst precursors **4 – 6** at different time intervals. The performance of each of catalyst precursor **4 – 6** was studied at different time intervals under the optimal catalytic conditions (75 °C

and 40 bar). A sample was taken and analysed by GC after 1, 2, 4 and 8 hours for each catalyst precursor. Figure 4 illustrates the conversion profile of the catalyst precursors with time.

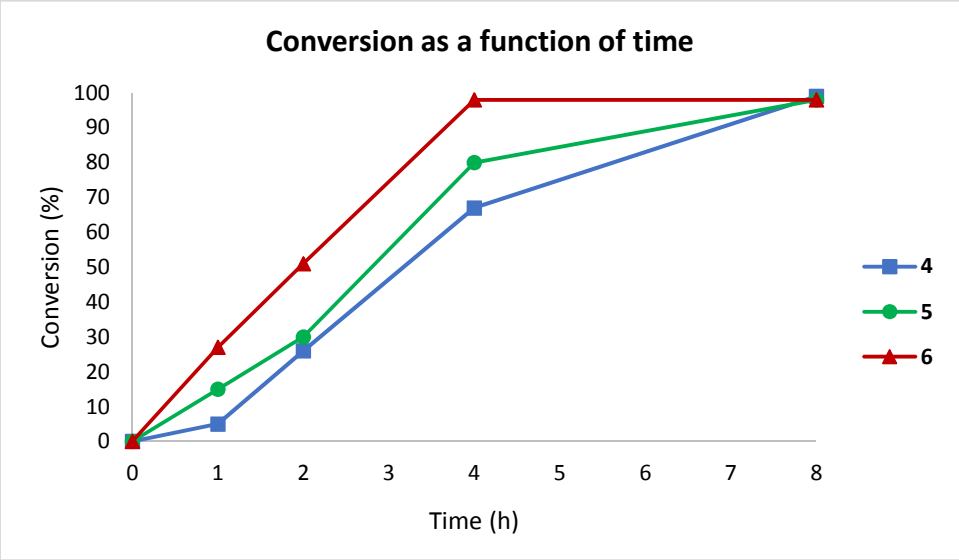


Figure 4: Conversion profile with time for catalyst precursors **4** – **6**.

The results show that at each time interval the trinuclear catalyst precursor (**6**) exhibits higher conversion than all the other, while the dinuclear catalyst precursor (**5**) exhibits higher conversion than the mononuclear catalyst precursor (**4**). When using **6** as a catalyst precursor, maximum conversion is achieved after 4 hours. This infers that the trinuclear complex exhibits a faster rate than the dinuclear complex which, in turn, exhibits a faster rate than the mononuclear complex during the catalytic reactions.

Recyclability and leaching studies

Recyclability studies were performed by cooling the reaction mixture to 0 °C and the toluene layer decanted. A fresh sample of 1-octene and *n*-decane dissolved in toluene was then added onto the aqueous layer and the hydroformylation reaction repeated. The results of the recyclability studies are shown in Figure 5. The catalysts could be recycled three times with the conversion of 1-octene decreasing drastically after each run for each catalyst precursor. The conversion had decreased to below 25 % by the third run. This decrease in conversion could be attributed to the low concentration of the catalyst precursors in the aqueous layer as a result of the catalyst precursors leaching into the organic layer.

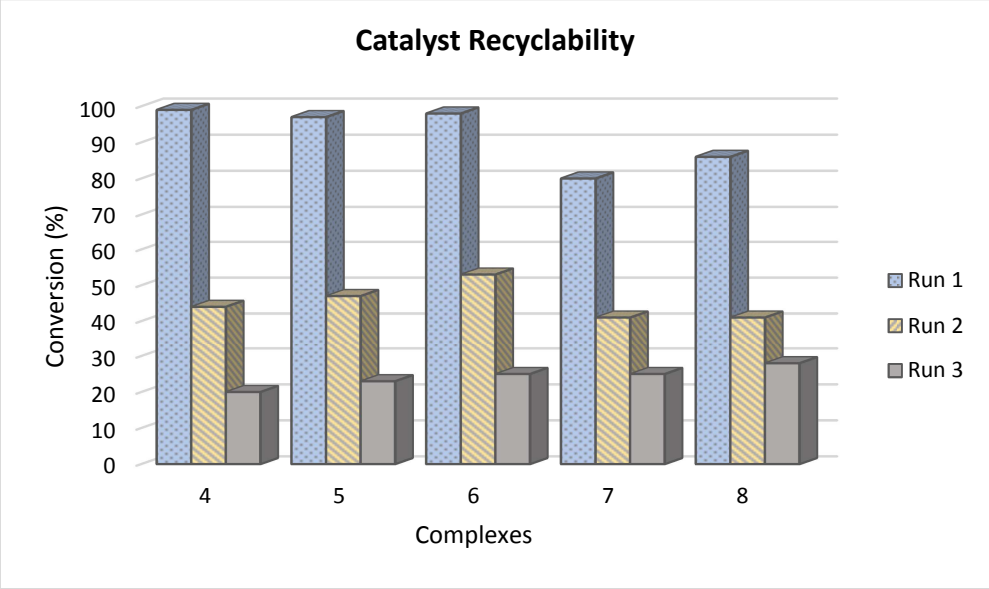


Figure 5: Recyclability studies of the catalysts at optimal conditions.

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to quantify the loss of the catalysts **4** – **8** into the organic layer by analysing the aqueous and organic layers of each catalyst before and after the hydroformylation reaction. The results show that more than 90 % of each catalyst leaches into the organic layer after the first run. These results corroborate the notion of leaching which then led to the observed significant drop in the conversion after the first run (Figure 5). The huge loss into the organic layer could be due to the catalyst precursors being soluble in toluene at elevated temperatures and pressures.

Mercury poisoning studies

Mercury poisoning studies were conducted as the need to suppress unwanted heterogeneous catalysts (nanoparticles) and thus determine whether the catalyst precursors are entirely homogeneous under the catalytic conditions is important. Free metal particles can be responsible for heterogeneous catalysis and therefore not giving a true reflection of the performance of the catalyst precursors as homogeneous catalysts. Mercury(0) is added to the catalytic reactions and can then form an amalgam with any free metal particles present, thus inhibiting the activity of the heterogeneous catalysts which may also exist as nanoparticles.

A drop of mercury was added to the reactor at the beginning of the hydroformylation reaction (t = 0 hours) and the catalytic reaction conducted under optimal conditions (75 °C and 40 bar) for 8 hours using each one of catalyst precursors **4** – **8**. The layers were then separated and the organic layer analysed using GC. Figure 6 shows the results obtained from these experiments. The conversion of 1-octene in the presence of mercury agrees (within experimental uncertainty) with the conversion of 1-octene obtained without mercury for all complexes employed. This suggests that only the molecular species is responsible for the conversions observed and not nanoparticles, thus all complexes (**4** – **8**) behave entirely as homogeneous catalysts under the catalytic conditions.

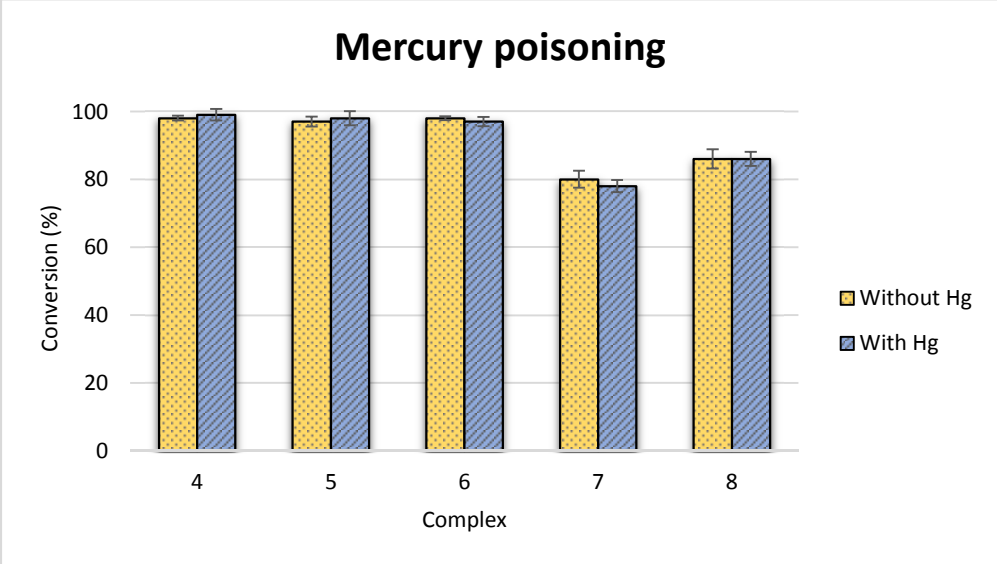


Figure 6: Comparison of 1-octene conversion in the absence and presence of mercury.

Conclusions

A series of mono-, di- and trinuclear Rh(I)-PTA complexes were synthesised and evaluated as catalyst precursors for the hydroformylation of 1-octene in an aqueous biphasic medium. All complexes were active in the hydroformylation of 1-octene to aldehydes, with TOF values over 200 h^{-1}. The COD complexes (**4** – **6**) proved to be more active than the CO complexes (**7** – **8**). Moreover, the COD complexes exhibit better chemoselectivity for aldehydes whilst The CO complexes exhibit better regioselectivity for linear aldehydes. This is due to the CO complexes not reaching quantitative conversion at 8 hours whereas all COD complexes reach quantitative conversion under the catalytic conditions. Increasing the number of metal centres had no significant effect on the chemo- and regioselectivity at 8 hours, but

studies of the catalyst precursors over time showed that increasing the number of metal centres increased the rate of the catalytic reaction. This is demonstrated by the trinuclear complex displaying a faster catalytic rate than the dinuclear complexes which, in turn, display faster rates than the mononuclear complexes. Mercury poisoning experiments confirmed that all the catalysts behave entirely as homogeneous catalysts when used for the aqueous biphasic hydroformylation of 1-octene. The complexes exhibited poor recyclability, attributed to significant leaching into the toluene layer. ICP-OES studies showed that *ca.* 90 % of each complex leaches into the toluene layer after the first run. The leaching could be as a result of the complexes being soluble in toluene under the catalytic conditions.

Experimental

Materials and methods

All reactions were carried out in an atmosphere of nitrogen unless otherwise stated. Solvents were dried and degassed prior to use. All chemicals were purchased from Sigma Aldrich and used as received, unless otherwise stated. $RhCl_3 \cdot 3H_2O$ was purchased from Heraeus South Africa. $[RhCl(COD)]_2$ dimer as well as ligands **1-3** were prepared according to previously reported procedures [32–34,39].

^{1}H NMR spectra were recorded on a Varian-300 MHz and $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ were recorded on a Varian-400 MHz (^{13}C: 101 MHz, ^{31}P: 162 MHz). Melting Points were obtained using a BÜCHI melting point apparatus B-540. Mass spectrometry was performed using a Waters Synapt G2 electron spray ionisation mass spectrometer in the positive or negative-ion mode at Stellenbosch University and elemental analyses was performed using a Thermos Scientific FLASH 2000 CHNS-O Analyzer at the University of Johannesburg. FT-IR spectra were recorded using Attenuated Total Reflectance Infrared spectroscopy (ATR-IR). Catalytic products were analysed and quantified using a Varian CP-8400 GC instrument. ICP-OES Varian 750-ES spectrophotometer was used to conduct inductively coupled plasma optical emission spectroscopy experiments

*General procedure for the synthesis of ligands **1' – 3'***

Either one of ligands **1** (101 mg, 0.356 mmol), **2** (199 mg, 0.407 mmol) or **3** (200. mg, 0.288 mmol) was dissolved in ethanol (50 mL). Appropriate equivalents of ammonium hexafluorophosphate (69.2 mg, 0.425 mmol for ligand **1'**; 140. mg, 0.859 mmol for ligands **2'** and 150. mg, 0.920 mmol for ligand **3'**) were added and the reaction mixture stirred at room temperature for 72 hours. The ligands precipitated out of solution as white solids which were isolated by suction filtration and dried under vacuum.

Ligand **1': Yield:** 231 mg, 83 %. **M.p.:** 145.4 – 146.6 °C. **^{1}H NMR** (DMSO–d_6, δ ppm): 7.67 – 7.44 (m, ^{3}J = 4.0 Hz, 5H, ArH), 5.04 – 4.82 (AB q, ^{2}J = 11.0 Hz, 4H, H_b), 4.47 – 4.33 (AB q, ^{2}J = 13.2 Hz, 2H, H_d), 4.22 (d, ^{2}J = 5.4 Hz, 2H, H_e), 4.07 (s, 2H, H_a), 3.93 – 3.76 (m, ^{2}J = 11.4 Hz, 4H, H_c). **^{13}C{^{1}H} NMR** (DMSO–d_6, δ ppm): 133.38 (C_g), 130.71 (C_i), 129.52 (C_h), 126.24 (C_f), 79.31 (C_b), 69.87 (C_d), 65.42 (C_a), 52.17 (C_e), 45.92 (C_c). **^{31}P{^{1}H} NMR** (DMSO–d_6, δ ppm): -83.50 (s, PTA), -144.18 (sept, ^{1}J = 711.3 Hz, PF_6). **ESI-MS(+)**: *m/z* 248.1320 $[M–PF_6]^+$. **Elemental Analysis**: $C_{13}H_{19}F_6N_3P_2$: Calcd. C 39.70, H 4.87, N 10.69 %. Found C 39.34, H 4.47, N 10.66 %. **$S_{20°C}$** = 4 mg/mL in H_2O.

Ligand **2': Yield:** 262 mg, 91 %. **M.p.**: 182.4 – 185.4 °C **^{1}H NMR** (DMSO–d_6, δ ppm): δ 7.61 (s, 4H, ArH), 5.06 – 4.85 (AB q, 8H, H_b), 4.59 – 4.33 (AB q, 4H, H_d), 4.24 (d, J = 4.4 Hz, 4H, H_e), 4.14 (s, 4H, H_a), 3.91 – 3.80 ppm (m, 8H, H_c). **^{13}C{^{1}H} NMR** (DMSO–d_6, δ ppm): 133.93 (C_g), 128.17 (C_f), 79.44 (s, C_b), 69.85 (s, C_d), 64.63 (s, C_a), 52.35 (d, C_e), 45.88 (d, C_c). **^{31}P{^{1}H} NMR** (DMSO–d_6, δ ppm): -83.63 (s, PTA), -144.17 (sept, ^{1}J = 711.2 Hz, PF_6). **ESI-MS(+)**: *m/z* 209.1084 $[M–2PF_6]^{2+}$. **Elemental Analysis**: $C_{20}H_{32}F_{12}N_6P_4$: Calcd. C 33.91, H 4.55, N 11.86 %. Found C 34.02, H 5.16, N 11.42 %. **$S_{20°C}$** = 5 mg/mL in H_2O.

Ligand **3': Yield:** 243 mg, 82 %. **M.p.:** 322.9 – 326.1 °C. **^{1}H NMR** (DMSO–d_6, δ ppm): 77.5 (s, 3H, ArH), 5.27 – 5.09 (AB q, ^{2}J = 11.0 Hz, 12H, H_b), 4.64 (d, ^{2}J = 4.8 Hz, 6H, H_e), 4.50 – 4.11 (m, ^{2}J = 16.5 Hz, 6H, H_d), 4.06 (s, 6H, H_a), 4.04 – 3.84 (m, 12H, H_c). **^{13}C{^{1}H} NMR** (DMSO–d_6, δ ppm): 139.16 (C_g), 128.23 (C_f), 78.85 (C_b), 69.71 (C_d), 64.47 (C_a), 51.78 (C_e), 45.58 (C_c). **^{31}P{^{1}H} NMR** (DMSO–d_6, δ ppm): -82.63 (s, PTA), -144.18 (sept., ^{1}J = 711.2 Hz, PF_6). **ESI-MS(+)**: *m/z* 366.6320 $[M–2PF_6]^{2+}$. **Elemental Analysis**: $C_{27}H_{45}F_{18}N_9P_6$: Calcd. C 31.68, H 4.43, N 12.32 %. Found C 32.09, H 5.18, N 11.92 %. **$S_{20°C}$** = 4 mg/mL in H_2O.

*Synthesis of the mononuclear Rh-PTA metal complex (**4**)*

The synthetic method reported by Hapiot and Gonsalvi [40] was followed (with minor modifications) in the synthesis of complex **6**. $[RhCl(COD)]_2$ (63.5 mg, 0.129 mmol) was dissolved in DCM (50 mL). Ligand **1'** (100. mg, 0.254 mmol) was then added and the reaction mixture stirred at room temperature for 1.5 hours, after which the solution was concentrated to *ca.* 10 mL. Cold pentane was then added affording complex **6** as a yellow precipitate which was then isolated by suction filtration and dried under vacuum. **Yield:** 159 mg, 98 %. **M.p.:** Decomposes without melting, onset at 164.9 °C. **^{1}H NMR** (DMSO–d_6, δ ppm): 7.57 - 7.50 (m, 4H, ArH), 5.07 – 4.87 (AB q, ^2J = 10.5 Hz, 4H, H_b), 4.77 (d, ^2J = 10.8 Hz, 1H, H_d), 4.51 – 4.47 (m, 5H, H_{cod}, H_d), 4.33 (d, 2H, H_e), 4.22 (s, 2H, H_a), 4.12 – 3.94 (m, 4H, H_c), 2.45 – 2.19 (m, 4H, H_{cod}), 2.02 – 2.00 (m, ^3J = 8.1 Hz, 4H, H_{cod}). **^{13}C{^{1}H} NMR** (DMSO–d_6, δ ppm): 133.39 (C_g), 130.83 (C_i), 129.85 (C_h), 128.88 (C_f), 126.12 (C_{cod}), 78.75 (C_b), 64.35 (C_d), 68.09 (C_a), 55.35 (C_e), 52.12 (C_c), 27.98 (C_{cod}). **^{31}P{^{1}H} NMR** (DMSO–d_6, δ ppm): -32.67 (d, $^1J_{Rh\text{-}P}$ = 136.0 Hz, PTA), -144.18 (sept., ^1J = 711.2 Hz, PF_6). **ESI-MS(+)**: *m*/*z* 264.1263 $[M–PF_6+Na]^{2+}$. **Elemental Analysis**: $C_{21}H_{31}ClF_6N_3P_2Rh$: Calcd. C 39.42, H 4.88, N 6.57 %. Found C 39.72, H 5.17, N 6.61 %. **$S_{40°C}$** = 3 mg/mL in H_2O.

*Synthesis of the 1,4-binuclear Rh-PTA metal complex (**5**)*

$[RhCl(COD)]_2$ (70.4 mg, 0.143 mmol) was dissolved in DCM (40 mL) and ligand **2'** (100. mg, 0.141 mmol) was then added. The reaction mixture was stirred at room temperature with ligand **2'** in suspension for 2 hours. Complex **7** was observed as a yellow solid precipitating out of solution. The complex was then isolated by suction filtration, washed with copious amounts of methanol to get rid of unreacted ligand **2'** and then dried under vacuum. **Yield:** 159 mg, 94%. **M.p.:** Decomposes without melting, onset at 286.2 °C. **^{1}H NMR** (DMSO–d_6, δ ppm): 7.67 (s, 4H, ArH), 5.09 – 5.05 (m, ^2J = 12.1 Hz, 8H, H_b), 4.91 – 4.75 (AB q, 4H, H_d), 4.54 – 4.50 (m, 8H, H_{cod}), 4.36 (d, 4H, H_e), 4.30 (s, 4H, H_a), 4.13 – 4.08 (m, 8H, H_c), 3.96 – 3.91 (m, 4H, H_{cod}), 2.41 – 2.15 (m, 8H, H_{cod}), 2.05 – 2.01 (m, 4H, H_{cod}). **^{13}C{^{1}H} NMR** (DMSO–d_6, δ ppm): 134.09 (C_f), 130.37 (C_g), 127.97 (C_{cod}), 79.14 (C_b), 68.14 (C_d), 63.49 (C_e), 54.70 (C_a), 51.87 (C_c), 27.90 (C_{cod}). **^{31}P{^{1}H} NMR** (DMSO–d_6, δ ppm): -32.17 (d, $^1J_{Rh\text{-}P}$ = 157.9 Hz, PTA), -144.18 (sept., ^1J = 711.2 Hz, PF_6). **ESI-MS(+)**: *m*/*z* 312.9192 $[M–2PF_6+Na]^{3+}$. **Elemental**

Analysis: $C_{36}H_{56}Cl_2F_{12}N_6P_4Rh_2$: Calcd. C 35.99, H 4.70, N 6.99 %. Found C 35.57, H 4.73, N 6.54 %. $\mathbf{S_{40°C}}$ = 1.5 mg/mL in H_2O.

*Synthesis of the trinuclear Rh-PTA metal complex (**6**)*

$[RhCl(COD)]_2$ (72.6 mg, 0.147 mmol) was dissolved in DCM (50 mL). Ligand **3'** (99.6 mg, 0.0973 mmol) was then added and the reaction mixture was stirred at room temperature for 24 hours. Complex **6** was observed as a yellow solid which was then isolated by suction filtration, washed with DCM and dried under vacuum. **Yield:** 105 mg, 61 %. **M.p.:** Decomposes without melting, onset at 359.4 °C. **^{1}H NMR** (DMSO–d_6, δ ppm): 7.72 (s, 3H, ArH), 5.31 – 5.13 (AB q, ^2J = 10.5 Hz, H_b), 4.77 – 4.54 (m, 12H, H_d), 4.48 – 4.44 (m, 18H, $H_{e,\,cod}$), 4.30 (s, 6H, H_a), 4.20 – 4.07 (m, ^2J = 14.5 Hz, 12H, H_c), 2.38 – 2.22 (m, 12H, H_{cod}), 2.01 – 1.91 (m, ^3J = 7.6 Hz, 6H, H_{cod}). **^{13}C{^{1}H} NMR** (DMSO–d_6, δ ppm): 138.33 (C_g), 128.45 (C_f), 126.89 (C_{cod}), 79.81 (C_b), 68.01 (C_d), 63.45 (C_a), 58.81 (C_e), 51.69 (C_c), 27.98 (C_{cod}). **^{31}P{^{1}H} NMR** (DMSO–d_6, δ ppm): -32.38 (d, $^1J_{Rh\text{-}P}$ = 145.5 Hz, PTA), -144.18 (sept., PF_6). **ESI-MS(+)**: *m*/*z* 476.9400 $[M–3PF_6]^{3+}$. **Elemental Analysis**: $C_{51}H_{81}Cl_3F_{18}N_9P_6Rh_3$: Calcd. C 34.74, H 4.63, N 7.15 %. Found C 34.63, H 4.97, N 7.75 %. $\mathbf{S_{40°C}}$ = 1 mg/mL in H_2O.

*General procedure for the synthesis of complexes **7** and **8***

Complex **4** (51.2 mg, 0.0800 mmol) and Complex **5** (200. mg, 0.166 mmol) were each dissolved in acetone (40 mL) and gaseous CO was bubbled through the solution at room temperature for 1 hour. The yellow solution gradually changed to orange. The solvent was then reduced and cold pentane added to afford Complexes **7** and **8** respectively as orange solids. The complexes were then each isolated by suction filtration, washed with pentane and dried under vacuum.

Complex **7: Yield:** 32.2 mg, 70 %. **M.p.:** Decomposes without melting, onset at 147.4 °C. **^{1}H NMR** (DMSO–d_6, δ ppm): 7.57 – 7.49 (m, 5H, ArH), 5.15 – 5.01 (AB q, 4H, H_b), 4.79 – 4.61 (AB q, 2H, H_d), 4.42 (d, 2H, H_e), 4.25 (s, 2H, H_a), 4.13 – 3.97 (m, 4H, H_c). **^{13}C{^{1}H} NMR** (DMSO–d_6, δ ppm): 192.08 (CO), 132.98 (C_g), 130.91 (C_i), 129.43 (C_h), 129.07 (C_f), 79.77 (C_b), 69.41 (C_d), 65.83 (C_a), 59.42 (C_e), 52.36 (C_c). **^{31}P{^{1}H} NMR** (DMSO–d_6, δ ppm): -33.44 (d, $^1J_{Rh\text{-}P}$ = 125.3 Hz, PTA), -144.18 (sept., ^1J = 711.3 Hz, PF_6). **FT-IR:** 2048 (CO), 1996 cm^{-1} (CO). **ESI-MS(+)**: *m*/*z*

248.1313 $[M–PF_6+Na]^{2+}$. **Elemental Analysis**: $C_{15}H_{19}ClF_6N_3O_2P_2Rh$: Calcd. C 30.66, H 3.26, N 7.15 %. Found C 30.80, H 3.71, N 7.79 %. $\mathbf{S_{40°C}}$ = 4 mg/mL in H_2O.

Complex **8: Yield:** 178 mg, 98 %. **M.p.:** Decomposes without melting, onset at 232.8 °C. **^{1}H NMR** (DMSO–d_6, δ ppm): 7.76 – 7.62 (m, 5H, ArH), 5.19 – 5.10 (m, 8H, H_b), 4.92 – 4.73 (m, 4H, H_d), 4.45 - 4.30 (m, 8H, $H_{a,e}$), 4.21 – 4.01 (m, 8H, H_c). **^{13}C{^{1}H} NMR** (DMSO–d_6, δ ppm): 193.77 (CO), 134.29 (C_g), 130.22 (C_f), 79.16 (C_b), 68.93 (C_d), 63.77 (C_a), 58.69 (C_e), 51.67 (C_c). **^{31}P{^{1}H} NMR** (DMSO–d_6, δ ppm): -20.93 (d, $^1J_{Rh\text{-}P}$ = 148.5 Hz, PTA), -144.17 (sept., ^1J = 711.3 Hz, PF_6). **FT-IR:** 1998 (CO), 2095 cm^{-1} (CO). **ESI-MS(+)**: *m/z* 268.1862 $[M–2PF_6+H]^{3+}$. **Elemental Analysis**: $C_{24}H_{32}Cl_2F_{12}N_6O_4P_4Rh_2$: Calcd. C 27.65, H 3.57, N 7.44 %. Found C 27.81, H 4.03, N 7.05 %. $\mathbf{S_{40°C}}$ = 2 mg/mL in H_2O.

General procedure for the Hydroformylation reactions

The hydroformylation reactions were carried out in a 90 mL stainless steel pipe reactor. The reactor was charged with toluene (5 mL), distilled water (5 mL) the substrate, 1-octene (805 mg, 7.18 mmol), the internal standard, n-decane (204 mg, 1.44 mmol) and either one of the Rh-PTA catalyst precursors **4** – **8** (Rh metal centre:substrate = 1:2500). The air-tight reactor was de-aerated by flushing twice with H_2 gas, then pressurised and heated to the desired syngas (CO:H_2, 1:1) pressure and temperature respectively. After 8 hours, the reactor was depressurised and the reaction transferred to a vial and cooled to 0 °C, the organic layer decanted and analysed using gas chromatography.

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Highlights

- Mono-, di- and trinuclear Rh(I) complexes based on alkylated-PTA scaffolds have been prepared.
- The complexes were characterized using several spectroscopic and analytical techniques.
- The complexes were evaluated as catalyst precursors for the hydroformylation of 1-octene.
- The trinuclear complex showed higher conversion rates.
- Poor recyclability was achieved.