Fréchet-type metallodendrons with N,P-iminophosphine Rh(I) complexes at the focal point: Synthesis and evaluation in the hydroformylation of 1-octene

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Abstract: Frêchet-type dendrons containing a chelating *N,P*-iminophosphine at the focal point were synthesized by reacting the *N,P*-iminophosphine Schiff base with the appropriate bromido-Frechet dendron (G_0, G_1 and G_2) via the Williamson-ether reaction. Neutral Rh(I) organmetallic dendrons were synthesized by reacting the *N,P*-iminophosphine dendron with $[Rh(\mu\text{-}Cl)(CO)_2]_2$. Th ligands and complexes were characterised using NMR and IR spectroscopy, mass spectrometry, elemental analysis and the G_0 analogue was characterised using single-crystal X-ray diffraction. All complexes were evaluated as catalyst precursors for the hydroformylation of 1-octene. In addition, chemoselectivity as a function of time (1 – 8 hrs) was conducted for the G_0-analogue. Mercury drop tests were performed using the G_0 analogue to determine the whether the catalysis mediated is homogenous, heterogeneous or a combination of both.

Introduction

Dendrimers represent a class of macromolecular constructs which have demonstrated applications in fields ranging from medicine to material science.[1] The discovery of dendrimers in the 1970's has stimulated interest into the study and synthesis of these versatile structures. Dendrimers are important synthons for the immobilisation of metals. The incorporation of metals into these scaffolds, allows for a further plethora of applications, which are predominantly used in catalytic, sensing and biomedical spheres.[2] The growing technological advances have instigated the need for specific materials with selectively controlled molecular architectures. To date, several metallodendrimers have been synthesised and characterised, presenting remarkable architectures in the chemistry landscape.

Core-functionalised metallodendrimers are often less explored due to the drawbacks associated with the synthesis and purification of these dendrons. There are fewer examples of dendrons with transition metals located at the focal point.[3] The paucity of literature on the synthesis of organometallic dendrons containing discrete rhodium(I) entities at the focal point prompted us to synthesise Fréchet-type organometallic dendrons with *N,O*-salicylaldimine Rh(I) complexes at the focal point (Figure 1).[3d] Recently, we reported on the use of these complexes as catalysts precursors in the hydroformylation reaction.[3d]

[Insert scheme 1 here]

Scheme 1. Previously reported synthesis of Fréchet-type organometallic dendrons with *N,O*-salicylaldimine Rh(I) complexes at the focal point.[3d]

The hydroformylation reaction, also known as the "Oxo process", is one of the most important industrial processes as it is estimated to produce 10 million tonnes of aldehydes annually.[4] This reaction is a transition metal-catalysed addition of carbon monoxide and hydrogen gas to olefins resulting in the formation of aldehydes. The homogeneous nature of the catalyst allows for superior activity and selectivity in comparison to heterogeneous counterparts.[5] Dendrimers aid in the stabilisation of metal complexes, by virtue of the microenvironment imparted by the dendritic architecture.[6] Most dendrimer scaffolds previously utilised in the hydroformylation reaction were based on DAB-PPI, PAMAM or carbosilane dendritic systems, with the metals located on either the periphery or interior cavities of these dendritic architectures.[7] Many of the dendrimers used in hydroformylation reactions are also anchored to organic or inorganic supports, thus in these cases the activity and selectivity of the catalysts are hampered due to their heterogeneous property.[6a, 8] As an extension to our previous studies based on *N,O*-salicylaldimine Fréchet-type dendritic scaffolds with rhodium at the focal point in the hydroformylation reaction, the current work is aimed at evaluating the effect of the *N,P*-chelating iminophosphine Rh(I) Frêchet dendrons on the hydroformylation reaction, using 1-octene as the model substrate.[3d]

Results and Discussion

Synthesis and characterization of Fréchet dendrons with *N,P*-iminophosphine ligands at the focal point.

The iminophosphine Schiff-base ligand was synthesized using modified literature methods (Scheme 2).[9] 2-Diphenylphosphinobenzaldehyde was reacted with 4-aminophenol via a Schiff-base condensation reaction to afford the imine product. The Schiff-base ligand was coupled with the bromido-Fréchet dendrons, *via* the Williamson-ether reaction to form ligands **1-3**. The coupling reaction using Schiff-bases is based on previous work done on the analogous *N,O*-

salicylaldimine series.[3d] Notably the coupling reaction involves the nucleophilic attack of the phenolic group onto the bromido-benzylic site of the Frêchet dendron.

[insert Scheme 2 here]

Scheme 2. Synthesis of *N,P*-iminophosphine dendrons (**1**-**3**) and *N,P*-iminophosphine organometallic dendrons with Rh(I)(CO)(Cl) moiety at the focal point (**4**-**6**). i) K_2CO_3, acetone, 18-C-6, reflux, 24-48 hrs. ii) $[Rh(\mu\text{-Cl})(CO)_2]_2$, 25 °C, dichloromethane.

The Schiff-base dendron products (1-3) were isolated as yellow solids in high yields. The ^{1}H NMR spectra confirmed the alkylation for compounds 1-3. From ^{1}H NMR, no phenolic signal (-OH) was observed at δ_H 9.66 ppm, which is indicative of the successful Williamson-ether reaction. Furthermore a shift of the bromo-methylene signal was observed which indicates that the nucleophilic attack had occurred at the reactive benzylic position to form the ether-linkage, this observation is in agreement with structurally similar dendrons.[3d] A small shift was observed for the imine signal which shows that there is no significant effect of the dendron on the electronics of the aryl imine. Notably an increase in generation size results in a similar effect. Peak broadening was observed for the higher generation dendrimer, which is expected due to the overlap of aryl-ether protons and inherent reduced tumbling of the macromolecule in solution as indicated by ^{1}H NMR spectroscopy.[3d]

In the ^{13}C NMR spectrum for compounds 1-3, the number of carbons resonances correlates to the proposed structures. In addition, compounds 1-3 were characterised using $^{31}P\{^1H\}$ NMR spectroscopy. A single resonance is observed in the $^{31}P\{^1H\}$ NMR spectrum at δ_P -13.25, -13.26 and -13.26 ppm for compounds 1, 2 and 3 respectively, thus attesting to the presence of a single phosphorous species. The compounds 1-3 display good stability in air with negligible oxidation observed for these phosphorous ligands. The absorption band for the imine moiety *v*(C=N) is observed in the IR spectra as an intense band between 1611 – 1617 cm^{-1}. Compound 1 was analysed using EI-MS. A molecular ion is observed at *m/z* 529.04 for compound 1. For the larger dendrons 2 and 3, MALDI-TOF-MS (+ve mode) was used to confirm the successful product formation. The parent ion $[M]^+$ is observed for these dendrons at *m/z* 799.86 and 1340.43 for compounds 2 and 3 respectively.

Synthesis and characterization of Fréchet dendrons with *N,P*-iminophosphine Rh(I)-(CO)(Cl) complexes at the focal point

The synthesis of the chloro-carbonyl containing Rh(I) organometallic dendrons 4 – 6 was accomplished by reacting the $[Rh(\mu\text{-Cl})(CO)_2]_2$ dimer with the appropriate *N,P*-iminophosphine dendron 1, 2 or 3 *via* a bridge splitting reaction and chelation. The complexes 4 – 6 were isolated as orange solids in high yields (92 – 96%).

The ^{1}H NMR spectra of complexes 4 – 6 displays a shift from δ_H 9.11 ppm to 8.02 – 8.05 ppm for the imine proton (HC=N) upon complexation. The magnitude of the shift is comparable to structurally similar *N,P*-iminophosphine Rh(I) complexes.[10] The multiplicity of the imine (HC=N) proton resonance could not be observed due to overlap with the aromatic dendritic proton resonances. The shift of the imine signal further confirms successful complexation to the imine nitrogen on rhodium. The proton signals for the methylene (-CH_2), methoxy (-OCH_3) and aryl-ether protons (Fréchet dendron) of the dendritic core occur at similar chemical shifts to those of the *N,P*-iminophosphine dendron ligands 1 - 3.

The bidentate coordination mode was confirmed using $^{31}P\{^1H\}$ NMR spectroscopy, as a downfield shift is observed from δ_P -13.2 to 48.5 ppm. The $^{31}P\{^1H\}$ NMR spectra shows a doublet with a coupling constant of 165 Hz ($^1J_{RhP}$) for complexes 4 – 6, this is comparable to structurally similar compounds reported in literature.[10] The presence of one doublet for complexes 4 – 6 attests to the formation of a single isomer for the complexes, in which the carbonyl is *cis* to the phosphorous atom. The magnitude of the coupling constant and the chemical shift for complexes 4 – 6 are comparable for structurally similar *cis*-isomers (carbonyl *cis* to phosphorous) reported in literature. Partial oxidation (4 – 7%) of the complex to the phosphine oxide of the ligands was observed. This was realised within 2 hours of running the $^{31}P\{^1H\}$ NMR of complexes 4 – 6. Hence the complexes were not stable in solution and were stored as solids under an inert atmosphere. The infrared spectra of complexes 4 – 6 displays a shift in the *v*(C=N) absorption band from approximately 1611 cm^{-1} to 1607 – 1609 cm^{-1}. This shift to lower wavenumbers supports the coordination of rhodium to the imine nitrogen.[10] A single carbonyl absorption band was observed at 1988, 1986 and 1990 cm^{-1} for complexes 4, 5 and 6 respectively. The wavenumber (1986 – 1990 cm^{-1}) suggests that these are terminal carbonyls, furthermore the occurrence of one absorption band (C≡O) further corroborates the presence of a single isomer in the solid state.[10] The wavenumber region (1986 – 1990 cm^{-1}) is indicative of the *cis* isomer, thus confirming the successful product formation. HR-ESI mass spectrometry was used to further confirm the structural integrity of the organometallic dendrons 4 – 6. The HR-ESI-MS analysis (recorded in the positive mode) of complexes 4 – 6 yielded $[M\text{-Cl}]^+$ fragments. These are *m/z* 660.0795, 930.1716 and 1470.3429 for complexes 4, 5 and 6 respectively. The molecular structure of complex 4 was confirmed by single crystal X-ray diffraction analysis (Figure 1). Single crystals were grown by a slow diffusion of pentane into a concentrated dichloromethane/toluene (*v/v*, 1:1) solution of complex 4.

[insert figure 1 here]

Figure 1. *ORTEP representation of complex 4, with thermal ellipsoids at the 50% probability level. Note hydrogen atoms are omitted for clarity. Atoms are labelled for referral in Table 1.*

Table 1. *Selected crystallographic information for complex 4.*

[insert table 1 here]

The geometry, bond length and angles are comparable to structurally similar *N,P*-iminophosphine Rh(I) complexes.[10-11] The full crystallographic data and structure refinement parameters of complex **4** can be found in Table 2.

[insert table 2 here]

Catalytic Evaluation of Complexes (4 – 6)

Using the optimised conditions for the previously reported *N,O*-salicylaldimine series, the effect of the *N,P*-donor atoms and dendron size were compared in the hydroformylation of 1-octene.[3d] The catalytic results with respect to chemoselectivity, regioselectivity and catalyst performance are discussed below (Table 3, *vide infra*).

Catalyst Performance

In general, the *N,O*-salicylaldimine complexes reported previously are superior than the *N,P*-iminophosphine complexes (**4** – **6**) with respect to activity under the tested hydroformylation conditions (Table 3).[3d] This seems to suggest that the *N,P*-iminophosphine Rh(I) complexes (**4** – **6**) may require an induction period, whereby more energy and/or time is required to reach the activated species and consequently hydroformylate the respective olefins. This induction period is often attributed to the diffusion of syngas in the reaction solvent and subsequent coordination of H_2 and CO to the rhodium site of complexes **4** – **6**.[10b] Furthermore, complexes **4** – **6** contain bulky phenyl groups on the phosphine atom, which could hinder the coordination CO and H_2 to rhodium.[10b] For complexes **4** – **6**, the rhodium ion is bonded to a chloride ligand, thus upon higher pressures of syngas, hydrogen chloride is formed, which may temporarily inhibit the hydroformylation of the substrate. This was observed in Wilkinson's study on Rh(I) halide aryl-phosphines used for the hydroformylation of various olefins.[12] This induction period is often observed for structurally similar *N,P*-iminophosphine Rh(I) complexes.[10, 12] Furthermore as noted earlier, the oxidation of the *N,P*-iminophosphine complexes **4** – **6** is observed with time, which may contribute to the deactivation of the catalyst and subsequent lower catalyst performance observed, however further investigation is required to understand this phenomenon. In the context of dendron size, the conversions of 1-octene across the dendron generations are comparable. Notably, no significant changes are observed for the aromatic proton signals of the Schiff-base moiety when comparing the characterisation data for the G_0 (**1**), G_1 (**2**) and G_2 (**3**) dendrons. Furthermore, the dendron is not a conjugated system, thus it does not affect the electronics of the catalyst system. For these reasons, the activity observed is comparable for the G_0, G_1 and G_2 Rh(I) dendrons **4** - **6**.

Table 3. The effect of dendron size, donor atoms and co-ligands (**4** – **6**) evaluated using the optimum conditions for the hydroformylation of 1-octene.

insert table 3 here]

a] The reactor was loaded with toluene (5 mL), 1-octene (0.805 g, 7.175 mmol), internal standard *n*-decane (0.204 mg, 1.435 mmol) and Rh-metal loading (2.87 x 10^{-3} mmol). The reactor was purged with nitrogen three times, followed by purging thrice with syngas. TOF = (mmol of aldehydes/mmol of Rh)/time. Catalyst to substrate ratio utilised was (1:2500). The samples were analysed using GC-FID. Reactions were conducted for 4 hours.

Chemoselectivity and Regioselectivity

Complexes **4** – **6** display chemoselectivity towards aldehydes. The chemoselectivity towards aldehydes for these complexes is comparable for structurally similar complexes in literature. [10, 13] [10, 13] [10, 13] [10, 13] [10, 13] 13, 14, 17 [13, 14, 17] [28-29, 32-34] In the context of regioselectivity, complexes **4** – **6** favour the formation of nonanal in comparison to the reported analogous salicylaldmine complexes (*n:iso* ratio of 2.08 vs 1.39 respectively).[3d] The hydroformylation precursors **4** – **6** possess bulky phosphine substituents, which imparts steric crowding around the metal centre and limits the isomerisation and/or alkene insertion under the conditions tested. Hence for this reason complexes **4** – **6** display enhanced regioselectivity in comparison to that of the *N,O*-salicylaldimine complexes. Interestingly, no hydroformylation of 4-octene to 2-propyl-hexanal was observed for complexes **4** – **6**. This evidence further demonstrates the steric-crowding observed for complexes **4** – **6**, which is observed for structurally similar bidentate phosphines in literature. In the context of dendron size, generally across the generation size (G_0, G_1, G_2) there is an increase in the chemoselectivity to form aldehydes for the hydroformylation precursors. This may be attributed to the bulkier nature (steric-effect) of the dendrons, which limits the isomerisation from terminal to internal alkenes. Similarly this was observed for the *N,O*-salicylaldimine series.[3d] A general trend observed across the dendron series (G_0 – G_2) is that the regioselectivity is consistent (**4** – **6**), see figure 2. One reason is that the dendron is presumed to be too far from the catalytic centre to impact on the regioselectivity of the hydroformylation reaction . Furthermore, the electronics is similar around the metal centre, which is reflected in the hydroformylation results.

[insert figure 2 here]

Figure 3. Graphical representation of chemoselectivity and regioselectivity of catalyst precursors 4-6.

Selectivity as a function of time

The chemoselectivity of the Rh(I) complexes (**4**) were evaluated at various times (Figure 3). This was conducted using the optimised conditions 75 °C and 30 bar. The precursor was evaluated at 1 hour, 2 hours, 4 hours and 8 hours respectively. Notably there is small increase in the chemoselectivity towards aldehydes.This observation indicates that the isomerisation products decrease as a function of time and consequently being hydroformylated to branched aldehydes. This observation is

confirmed when evaluating the regioselectivity as a function of time. The *n:iso* ratio decreases as a function of time, further providing evidence that the *iso*-octenes are being hydroformylated to *iso*-aldehydes at longer reaction times. Further inspection of the distribution of iso-octenes shows that a significant quanitity of 4-octene is still present. In comparison to the *N,O*-salicylaldimine counterparts this is an interesting feature as in the *N,O*-salicylaldimine case, no iso-octenes were present after 8hrs. This demonstrates the catalysts potential for increasing the selectivity towards linear aldehydes.

[insert figure 3 here]

Figure 4. Chemoselectivity as a function of time

Mercury poisoning experiments

A useful method for differentiating between homogeneous and heterogeneous catalysis is mercury drop experiments.[5b, 14] If nanoparticles are formed in solution, the introduction of mercury results in the formation of an amalgam between mercury and the metal-nanoparticles. This amalgam is not active in the hydroformylation reaction, thus a poisoning of the catalytic system results in a drop in the catalytic activity if nanoparticles were present. The reactions were performed using the temperature (75 °C), time (8 hours) and pressure (30 bar) in the presence of mercury. A drop in conversion is observed for complex **4** (Figure 4). This suggests that the conversion is attributed to a combination of heterogeneous and homogeneous catalysis. This could be attributed to the oxidation of the phosphorous ligand in solution (as discussed in earlier). The formation and accumulation of colloidal particles are often associated with the increase in the rate of isomerisation, which is further observed in the catalytic results.[3d]

[insert figure 4here]

Conclusions

The analogous series of Fréchet-type metallodendrons with *N,P*-iminophosphine Rh(I) complexes at the focal point were synthesized and characterised using analytical and spectroscopic methods. The ligands (**1-3**) were constructed using the Williamson-ether synthesis. Complexation was accomplished using $[Rh(\mu\text{-}Cl)(CO)_2]_2$ to afford the Fréchet-type metallodendrons with *N,P*-iminophosphine Rh(I) complexes at the focal point. The complexes (**4-6**) were stable as solids at room temperature under inert atmosphere. The organometallic complexes were evaluated in the hydroformylation of 1-octene using optimised conditions of an analogous *N,O*-salicylaldimine Fréchet-type metallodendron series. The complexes tested were active in the hydroformylation reaction, the complexes displayed low conversions, moderate chemoselectivity and good regioselectivity in comparison to the *N,O*-salicylaldimine Fréchet-type metallodendron series. The low conversions may be attributed to the decomposition of the complexes under hydroformylation conditions. Mercury drop experiments were performed using G_0-analogue. Notably a decrease in conversion was observed which indicates the hydroformylation activity for this class of compounds is a combination of homogeneous catalysis and catalysis facilitated by nanoparticles formed in solution. `

Experimental Section

General: All reagents were purchased from Sigma-Aldrich and Acros Organics. Rhodium(III) trichloride trihydrate was purchased from Heraeus SA. All solvents were dried using 3Å molecular sieves and degassed using the freeze-thaw-pump method. The rhodium chloro-carbonyl dimer $[Rh(\mu\text{-}Cl)(CO)_2]_2$,[15] Fréchet dendrons[16] and (E)-4-((2-(diphenylphosphanyl)benzylidene)amino)phenol[9] were prepared by means of published methods. Nuclear magnetic resonance (NMR) spectra were recorded on either a Bruker Topsin GmbH 400 plus (^{1}H: 400.22 MHz; $^{13}C\{^1H\}$: 100.65 MHz; $^{31}P\{^1H\}$: 162.01 MHz) or a Varian Mercury 300 (^{1}H: 300.08 MHz; $^{13}C\{^1H\}$: 75.46 MHz; $^{31}P\{^1H\}$: 121.47 MHz) spectrometer. These were equipped with a Bruker Biospin GmbH casing and sample injector at 30 °C. Chemical shifts for ^{1}H and $^{13}C\{^1H\}$ NMR were reported using tetramethylsilane (TMS) as the internal standard. Infrared (IR) absorptions were measured on a Perkin-Elmer Spectrum 100 FT-IR spectrometer using Attenuated Total Reflectance Infrared spectroscopy (ATR-IR). Electron impact mass spectrometry (EI-MS) was conducted using a JEOL GCMateII mass spectrometer. Low resolution and high resolution (HR) electrospray ionisation mass spectrometry (ESI-MS) was carried out on a Waters API Quattro mass spectrometer, with scans being conducted in the positive mode. Matrix assisted laser desorption time-of-flight (MALDI-TOF) mass spectra were carried out on a Bruker Daltronics Ultraflex 2 equipped with a nitrogen laser and operated at an accelerating voltage of 25 kV. The matrix utilised was 2,5-dihydroxybenzoic acid (6.5 mM). Elemental analysis (C, H, N) were performed using a Fissions EA 110 CHNS apparatus or an Elementar Vario EL Cube Analyser. Some of the data obtained are outside acceptable limits, this can be ascribed to the presence of solvent molecules due to the encapsulation. This is a common observation for dendritic molecules.[3d, 17] Melting Points were determined using a Büchi melting point apparatus B-540 and are uncorrected.

Fréchet dendrons with *N,P*-iminophosphine ligand precursors at the focal point (1 – 3)

General Method

(*E*)-4-((2-(diphenylphosphanyl)benzylidene)amino)phenol (2.0 eq.), potassium carbonate (1.0 – 1.5 eq.) and 18-crown-ether (0.2 eq.) were dissolved in anhydrous acetone (30 mL) and refluxed for 1 hour. To this, a solution of the appropriate Fréchet dendron with a benzyl bromide focal point (1.0 eq.) in dry acetone (20 mL) was added dropwise. The resultant mixture was further refluxed for an additional 23 hours. The mixture was cooled to room temperature and evaporated to dryness under reduced pressure. The residue was partitioned between water (10 mL) and dichloromethane (10 mL), and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The organic fractions were combined and collected. The combined organic fractions were dried using anhydrous magnesium sulfate. After removal of the drying agent by filtration, the solvent was removed to yield a brown residue. The crude product was purified as outlined in the following text for the respective ligands **1 – 3**.

Synthesis and characterisation of the G_0-COOMe-*N,P*-iminophosphine dendron (1).

(E)-4-((2-(diphenylphosphanyl)benzylidene)amino)phenol (500 mg, 1.31 mmol, 2.00 eq.), potassium carbonate (226 mg, 1.64 mmol, 1.00 eq.), 18-crown-ether (15.0 mg, 0.056 mmol, 0.200 eq.) and the G_0-Br dendron (150 mg, 0.656 mmol, 1.00 eq.) were reacted in degassed anhydrous acetone. The residue was dissolved in chloroform and precipitated with petroleum ether. The resultant crystalline solids were filtered and washed with cold chloroform to yield the product (1) as a yellow crystalline solid. Yield: 330 mg (95%). IR (ATR, cm^{-1}): 1720 (sharp, strong, C=O), 1613 (sharp, medium, C=N). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.11 (d, $^4J_{HP}$ = 5.2 Hz, 1H, H_{imine}), 8.22 (ddd,$^3J_{HH}$ = 7.7, $^4J_{HP}$ = 3.9, $^4J_{HH}$ = 1.2 Hz, 1H, H_{ar}), 8.08 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_{ar}), 7.52 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_{ar}), 7.45 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 0.72 Hz, 1H, H_{ar}), 7.41 – 7.29 (m, 11H, H_{ar}), 7.01 – 6.88 (m, 5H, H_3, H_{ar}), 5.13 (s, 2H, H_{CH2}), 3.95 (s, 3H, H_{CH3}). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 166.95 (s, C_{Ar}), 157.30 (d, $^3J_{CP}$ = 21.7 Hz, C_{imine}), 157.20, (s, C_{Ar}), 157.17 (s, C_{Ar}), 145.26 (s, C_{Ar}), 142.35 (s, C_{Ar}), 139.57 (d, $^1J_{CP}$ = 16.8 Hz, C_{Ar}), 138.46 (d, $^1J_{CP}$ = 20.0 Hz, C_{Ar}), 136.70 (d, $^2J_{CP}$ = 9.6 Hz, C_{Ar}), 134.20 (d, $^2J_{CP}$ = 20.0 Hz, C_{Ar}), 133.71 (s, C_{Ar}), 130.76 (s, C_{Ar}), 130.02 (s, C_{Ar}), 129.08 (s, C_{Ar}), 129.03(s, C_{Ar}), 128.78 (d, $^2J_{CP}$ = 7.2 Hz, C_{Ar}), 128.11 (d, $^3J_{CP}$ = 3.9 Hz, C_{Ar}), 127.08 (s, C_{Ar}), 122.50 (s, C_{Ar}), 115.40 (s, C_{Ar}), 69.73 (s, C_{CH2}), 52.24 (s, C_{CH3}).^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): -13.25 (s). Elemental Analysis for $C_{34}H_{28}NO_3P$ (529.1807): C, 77.11; H, 5.33; N, 2.64; Found: C, 76.88; H, 5.00; N, 2.26%. EI-MS (m/z): 529.0436 $[M]^+$. Melting Point: 131.4 – 132.9 ˚C.

Synthesis and characterisation of the G_0-COOMe-*N,P*-iminophosphine dendron (2).

(E)-4-((2-(diphenylphosphanyl)benzylidene)amino)phenol (500 mg, 1.31 mmol, 2.00 eq.), potassium carbonate (227 mg, 1.64 mmol, 2.50 eq.), 18-crown-ether (43.3 mg, 0.163 mmol, 0.200 eq.) and the G_1-Br dendron (65 mg, 0.281 mmol, 1.00 eq.) were reacted in degassed anhydrous acetone. The residue was dissolved in chloroform and precipitated with petroleum ether. The residue was triturated with diethyl ether, filtered and dried *in vacuo* to yield the product (2) as a yellow powder. Yield: 456 mg (87%). IR (ATR, cm^{-1}): *v* = 1714 (sharp, strong, C=O), 1611 (sharp, medium, C=N). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (d, $^4J_{HP}$ = 5.2 Hz, 1H, H_{imine}), 8.20 (ddd,$^3J_{HH}$ = 7.7 Hz, $^4J_{HP}$ = 3.3 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H_{Ar}), 8.05 (d, $^3J_{HH}$ = 8.2 Hz, 4H, H_{Ar}), 7.52 – 7.41 (m, 5H, H_{Ar}), 7.38 – 7.28 (m, 11H, H_{Ar}), 6.95 (m, 3H, H_{Ar}), 6.88 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H_{Ar}), 6.67 (d, $^4J_{HH}$ = 2.0 Hz, 2H, H_{Ar}), 6.54 (t, $^4J_{HH}$ = 2.0 Hz, 1H, H_{Ar}), 5.10 (s, 4H, H_{CH2}), 4.98 (s, 2H, H_{CH2}), 3.92 (s, 6H, H_{CH3}). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.94 (s, C_{Ar}), 160.07 (s, C_{Ar}), 157.80 – 156.65 (m, C_{Ar}, C_{imine}), 145.17 (s, C_{Ar}), 142.10 (s, C_{Ar}), 139.93 (s, C_{Ar}), 139.76 (s, C_{Ar}), 138.45 (d, $^1J_{CP}$ = 19.9 Hz, C_{Ar}), 136.76 (d, $^2J_{CP}$ = 9.7 Hz, C_{Ar}), 134.21 (d, $^2J_{CP}$ = 20.0 Hz, C_{Ar}), 133.73 (s, C_{Ar}), 130.73 (s, C_{Ar}), 130.04 (s, C_{Ar}), 129.95 (s, C_{Ar}), 129.09 (s, C_{Ar}), 129.03 (s, C_{Ar}), 128.79 (d, $^3J_{CP}$ = 7.1 Hz, C_{Ar}), 128.12 (d, $^3J_{CP}$ = 3.8 Hz, C_{Ar}), 127.14 (s, C_{Ar}), 122.47 (s, C_{Ar}), 115.44 (s, C_{Ar}), 106.65 (s, C_{Ar}), 101.85 (s, C_{Ar}), 70.20 (s, C_{CH2}), 69.65 (s, C_{CH2}), 52.25 (s, C_{CH3}).^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): -13.26 (s). Elemental Analysis for $C_{50}H_{42}NO_7P{\cdot}1.5\ H_2O$ (799.2699): C, 72.63; H, 5.49; N, 1.69; Found: C, 72.32; H, 5.31; N, 3.25%. MALDI-TOF-MS (+ve) (m/z): 800.2130 $[M + H]^+$. Melting Point: 132.4 – 134.4 ˚C.

Synthesis and characterisation of the G_0-COOMe-*N,P*-iminophosphine dendron (3).

E)-4-((2-(diphenylphosphanyl)benzylidene)amino)phenol (75.0 mg, 0.198 mmol, 2.00 eq.), potassium carbonate (34.2 mg, 0.247 mmol, 2.50 eq.), 18-crown-ether (6.54 mg, 0.0248 mmol, 0.250 eq.) and the G_2-Br dendron (103 mg, 0.100 mmol, 1.00 eq.) were reacted in degassed anhydrous acetone. The residue was triturated with anhydrous methanol, filtered and dried *in vacuo* to yield the product (2.13) as a pale yellow powder. Yield: 117 mg (88%). IR (ATR, cm^{-1}): *v* = 1714 (sharp, strong, C=O), 1611 (sharp, medium, C=N). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (d, $^4J_{HP}$ = 5.2 Hz, 1H, H_{imine}), 8.18 (ddd,$^3J_{HH}$ = 7.8, $^4J_{HP}$ = 3.9, $^4J_{HH}$ = 1.1 Hz, 1H, H_{Ar}), 8.03 (d, $^3J_{HH}$ = 8.2 Hz, 8H, H_{Ar}), 7.50 – 7.41 (m, 9H, H_{Ar}), 7.37 – 7.28 (m, 11H, H_{Ar}), 6.96 – 6.85 (m, 5H, H_{Ar}), 6.66 (d, $^4J_{HH}$ = 2.0 Hz, 4H, H_{Ar}), 6.64 (d, $^4J_{HH}$ = 2.0 Hz, 2H, H_{Ar}), 6.53 (t, $^4J_{HH}$ = 2.0 Hz, 2H, H_{Ar}), 6.51 (t, $^4J_{HH}$ = 2.0 Hz, 1H, H_{Ar}), 5.09 (s, 8H, H_{CH2}), 4.97 (s, 6H, H_{CH2}), 3.91 (s, 12H, H_{CH3}). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.92 (s, C_{Ar}), 160.17 (s, C_{Ar}), 160.07 (s, C_{Ar}), 157.36 - 156.97 (m, C_{Ar} and C_{imine}), 145.11 (s, C_{Ar}), 142.09 (s, C_{Ar}), 139.75 (s, C_{Ar}), 139.69 (s, C_{Ar}), 138.45 (d, $^1J_{CP}$ = 20.0 Hz, C_{Ar}), 136.77 (d, $^2J_{CP}$ = 9.6 Hz, C_{Ar}), 134.20 (d, $^2J_{CP}$ = 20.0 Hz, C_{Ar}), 133.74 (s, C_{Ar}), 130.73 (s, C_{Ar}), 130.04 (s, C_{Ar}), 129.94 (s, C_{Ar}), 129.09 (s, C_{Ar}), 129.03 (brs, C_{Ar} and C_{Ar}), 128.79 (d, $^3J_{CP}$ = 7.2 Hz, C_{Ar}), 128.14 (s, C_{Ar}), 127.13 (s, C_{Ar}), 122.47 (s, C_{Ar}), 115.44 (s, C_{Ar}), 106.69 (s, C_{Ar}), 106.52 (s, C_{Ar}), 101.91 (s, C_{Ar}), 101.79 (s, C_{Ar}), 70.29 (s, C_{CH2}), 70.05 (s, C_{CH2}), 69.64 (s, C_{CH2}), 52.24 (s, C_{CH3}). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): -13.29 (s). Elemental Analysis for $C_{82}H_{70}NO_{15}P{\cdot}4H_2O$ (1339.4483): C, 71.29; H, 5.69; N, 1.01; Found: C, 71.13; H, 5.77; N, 0.68%. MALDI-TOF-MS (+ve) (m/z): 1340.4801 $[M + H]^+$. Melting Point: 130.3 – 133.5 ˚C.

Rhodium(I) Carbonyl Chlorido-*N,P*-Iminophosphine Organometallic dendrons (4 – 6)

General Method

The *N,P*-iminophosphine ligands (**1, 2** or **3**) was stirred in a degassed solution of dichloromethane. To this, $[Rh(\mu\text{-}Cl)(CO)_2]_2$ was added which immediately resulted in a colour change of the solution from yellow to red. The reaction was stirred for 1 hour and monitored by TLC analysis. The solution was added to a silica-packed column, and eluted with Ethyl Acetate under a flow of argon. The product associated with the bright orange band was collected. The combined fractions were reduced *in vacuo* to yield the desired complex.

Synthesis and characterisation of the G_0-*N,P*-COOMe Rh(CO)(Cl) organometallic dendron (4).

Compound **1** (100 mg, 0.189 mmol, 1.00 eq.) was reacted with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (37.4 mg, 0.0963 mmol, 0.510 eq.). Complex **4** was isolated as an orange powder. Yield: 126 mg (96 %). IR (ATR, cm^{-1}): *v* = 1988 (sharp, strong, C≡O), 1720 (sharp, strong, C=O), 1609 (sharp, medium, C=N). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 – 7.91 (m, 3H, H_{imine} and H_{Ar}), 7.56 – 7.32 (m, 15H, H_{Ar}), 7.21 – 7.16 (m, 2H, H_{Ar}, overlap with $CDCl_3$), 6.91 (dd, $^3J_{HH}$ = 8.9 Hz, $^3J_{HH}$ 8.5 Hz, 1H, H_{Ar}), 6.82 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H_{Ar}), 5.02 (s, 2H, H_{CH2}), 3.85 (s, 3H, H_{CH3}).^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): 48.52 (d, $^1J_{RhP}$ = 165.2 Hz). Elemental Analysis for $C_{35}H_{28}NO_4ClPRh$ (695.0500): C, 60.40; H, 4.06; N, 2.01; Found C, 60.03; H, 4.12; N, 1.65%. HR-ESI-MS (m/z): 696.0754 $[M]^+$, 660.0795 $[M\text{-}Cl]^+$. Melting Point: Decomposes with melting, onset occurs at 213.6 °C.

Synthesis and characterisation of the G_1-*N,P*-COOMe Rh(CO)(Cl) organometallic dendron (5).

Compound **2** (100 mg, 0.125 mmol, 1.00 eq.) was reacted with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (24.8 mg, 0.0638 mmol, 0.510 eq.). Complex **5** was isolated as an orange powder. Yield: 114 mg (94 %). IR (ATR, cm^{-1}): *v* = 1986 (sharp, strong, C≡O), 1720 (sharp, strong, C=O), 1607 (sharp, medium, C=N). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (m, 5H, H_{imine} and H_{Ar}), 7.53 (m, 17H, H_1, H_{Ar}), 7.30 (m, 2H, H_{Ar}, overlap with $CDCl_3$), 7.05 – 6.95 (m, 1H, H_{Ar}), 6.89 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H_{Ar}), 6.67 (d, $^4J_{HH}$ = 2.2 Hz, 2H, H_{Ar}), 6.56 (t, $^4J_{HH}$ = 2.2 Hz, 1H, H_{Ar}), 5.12 (s, 4H, H_{CH2}), 4.99 (s, 2H, H_{CH2}), 3.94 (s, 6H, H_{CH3}). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): 48.51 (d, $^1J_{RhP}$ = 165.2 Hz). Elemental Analysis for $C_{51}H_{42}NO_8ClPRh{\cdot}7H_2O$ (965.1392): C, 56.08; H, 5.17; N,

1.28; Found: C, 56.50; H, 5.55; N, 0.98; %. HR-ESI-MS (m/z): 930.1716 $[M\text{-}Cl]^+$. Melting Point: Decomposes with melting, onset occurs at 161.9 °C

Synthesis and characterisation of the G_2-*N,P*-COOMe Rh(CO)(Cl) organometallic dendron (6).

Compound **3** (100 mg, 0.0746 mmol, 1.00 eq.) was reacted with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (15.1 mg, 0.0388 mmol, 0.510 eq.). Complex **6** was isolated as an orange amorphous solid. Yield: 104 mg, (93 %). IR: (ATR, cm^{-1}) 1990 (sharp, strong, C≡O), 1720 (sharp, strong, C=O), 1609 (sharp, medium, C=N). ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (m, 9H, H_{imine} and H_{Ar}), 7.51 (m, 21H, H_{Ar}), 7.30 – 7.09 (m, 3H, H_{Ar}, overlap with $CDCl_3$), 6.91 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H_{Ar}) 6.70 – 6.56 (m, 9H, H_{Ar}), 5.12 (s, 8H, H_{CH2}), 4.99 (s, 6H, H_{CH2} and H_{CH2}), 3.94 (s, 12H, H_{CH3}). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): 48.46 (d, $^1J_{RhP}$ = 165.2 Hz). Elemental Analysis $C_{83}H_{70}NO_{16}ClPRh \cdot 11H_2O$ (1505.3176): C, 58.47; H, 5.44; N, 0.88; Found C, 58.70; H, 5.81; N, 1.03;%. HR-ESI-MS (m/z): 1470.3429 $[M\text{-}Cl]^+$. Melting Point: Decomposes with melting, onset occurs at 117.3 °C

Single-crystal X-ray crystallography methods

Single-crystal X-ray diffraction data for compound **4** were collected using a Bruker Kappa APEX II DUO diffractometer equipped with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The temperature was controlled by an Oxford Cryostream cooling system (Oxford Cryostat), data collection was carried out at 100 (2) K. Cell refinement and data reduction were achieved using the program SAINT.[18] The data were scaled, and absorption correction was accomplished using SADABS.[19] The structure was solved by direct methods by using SHELXS-9733 and refined by full-matrix least-squares methods based on F^2 using SHELXL-9733.[20] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in idealised positions and refined in riding models with U_{iso} assigned 1.2 or 1.5 times U_{eq} of their parent atoms and the C-H bond distances were constrained from 0.95 to 0.99 Å. The programs X-Seed, Mercury and POV-Ray were used to produce ORTEP images of compound **4**.[19]

General method for the hydroformylation reaction

The hydroformylation reactions were performed in a 90 mL stainless steel pipe reactor equipped with a Teflon-coated magnetic stirrer bar. The reactor was charged with toluene (5 mL), 1-octene (7.175 mmol), internal standard n-decane (1.26 mmol) and Rh-metal loading (2.87 x 10-3 mmol). The pipe reactor was purged with nitrogen three times, followed by purging with syngas (1:1, CO: H_2) three times. The reactor was pressurised to the desired pressure and consequently heated to the desired temperature. Samples were collected at the beginning and at the end of each reaction. All reactions were performed in duplicate and are recorded as an average of two identical experiments.

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Keywords: Metallodendrons • Rhodium • Iminophosphine • Organometallic • Hydroformylation

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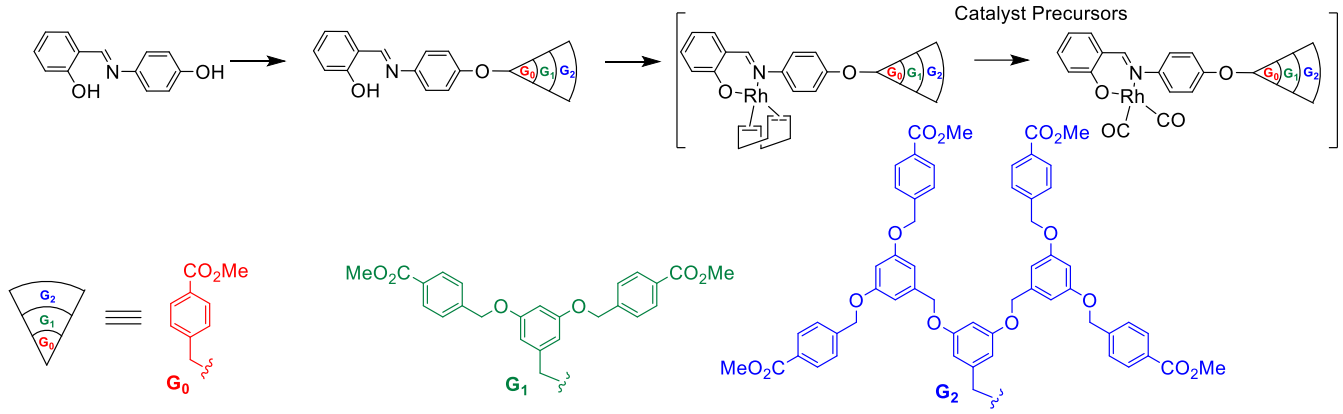
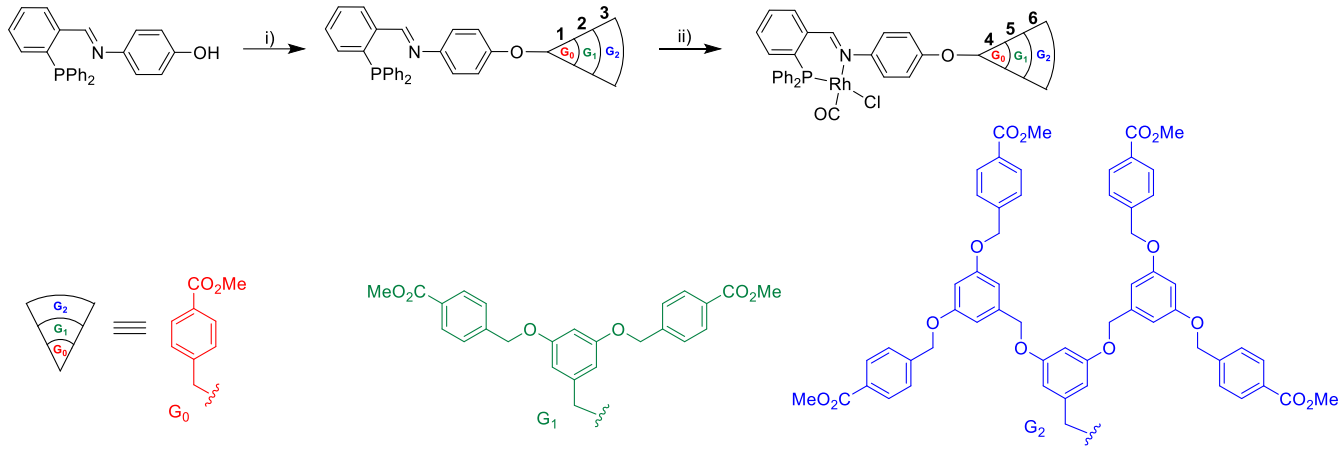


Scheme 1.



Scheme 2.

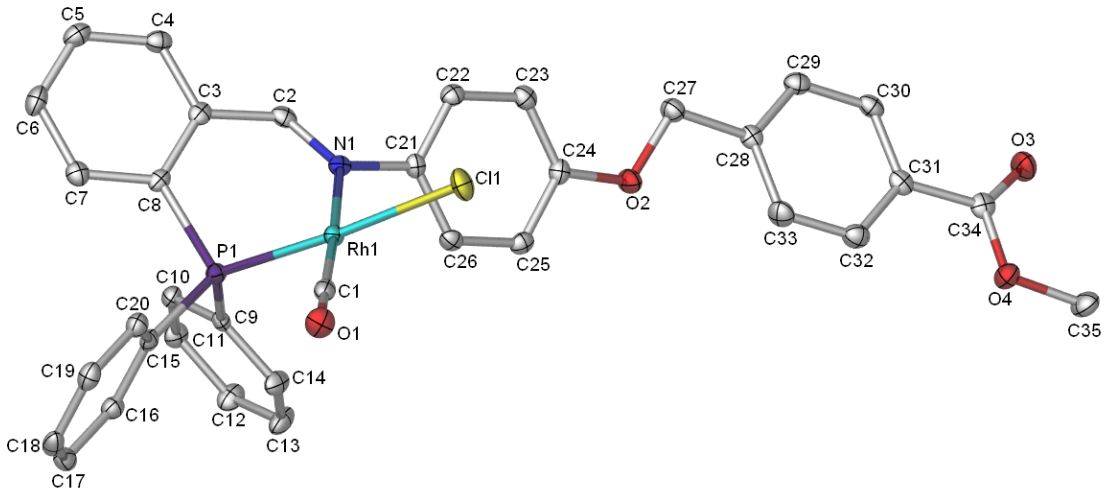


Figure 1.

Table 1.

Selected Bond Lengths	Interatomic distances (Å)
Rh1-N1	2.119(2)
Rh1-P1	2.2020(8)

Rh1-Cl1	2.3892(8)
Rh1-C1	1.820(3)
N1-C2	1.291(4)
C1-O1	1.149(3)
Selected Bond Angles	**Angles (°)**
N1-Rh1-P1	83.60(6)
N1-Rh1-Cl1	90.84(6)
C1-Rh1-Cl1	89.5(1)
C1-Rh1-P1	96.0(1)
P1-Rh1-Cl1	174.35(3)
N1-Rh1-C1	176.1(1)

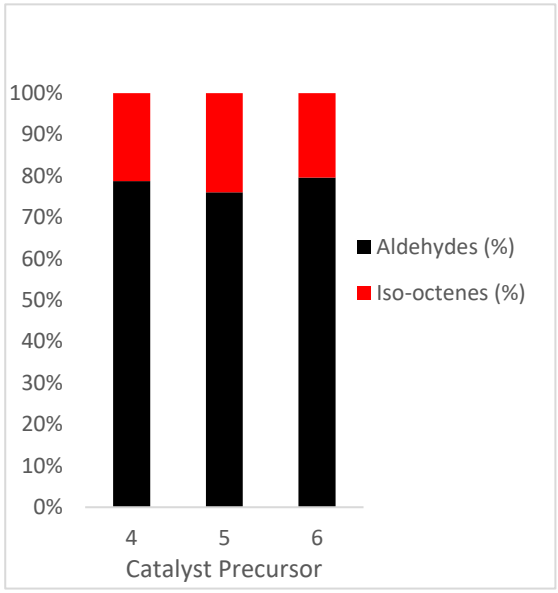
Table 2.

	4
Empirical Formula	$C_{35}H_{28}ClNO_4PRh$
Formula weight / g.mol^{-1}	695.91
Crystal system	Monoclinic
Space group	*P2$_1$/n*
Crystal colour and shape	Red block
Crystal size	0.03 x 0.07 x 0.12
a / Å	13.5854(8)
b / Å	10.4098(6)
c / Å	21.5335(12)
α / °	90
β / °	100.4050(10)
γ / °	90
V / Å^3	2995.22
Z, Z'	Z: 4 Z':0
T / K	100(2)
D_c / g.cm^{-1}	1.543
μ / mm^{-1}	0.754
Reflections used [I> 2s(I)]	6109
R_{int}	24389, 6109, 0.047
Final R indices [I > 2s(I)]	4484
R indices (all data)	0.0607
Goodness-of-fit	1.021
Max, Min Δρ/e Å^{-3}	-0.58, 0.53

Table 3. *The effect of dendron size, donor atoms and co-ligands (**4** – **6**) evaluated using the optimum conditions for the hydroformylation of 1-octene.*

	Conversion (%)	**Total Ald. (%)**	**Total (%)**	***Iso*-oct.**	**Linear Ald. (%)**	***Iso*-Ald. (%)**	***n:iso***	**TOF (h^{-1})**
4	4.56	78.77	21.23		66.90	33.10	2.02	22
5	4.95	76.09	23.91		67.51	32.49	2.08	24
6	7.56	79.59	20.41		64.07	35.93	1.78	38

The reactor was loaded with toluene (5 mL), 1-octene (0.805 g, 7.175 mmol), internal standard *n*-decane (0.204 mg, 1.435 mmol) and Rh-metal loading (2.87 x 10^{-3} mmol). The reactor was purged with nitrogen three times, followed by purging thrice with syngas. TOF = (mmol of aldehydes/mmol of Rh)/time. Catalyst to substrate ratio utilised was (1:2500). The samples were analysed using GC-FID. Reactions were conducted for 4 hours.



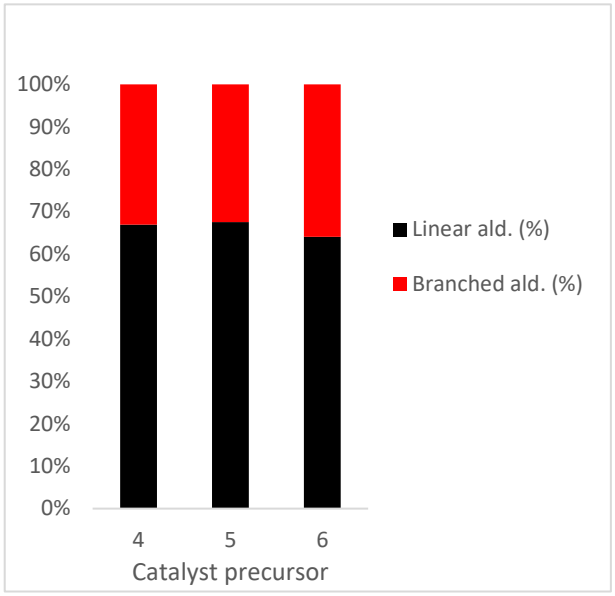


Figure 2.

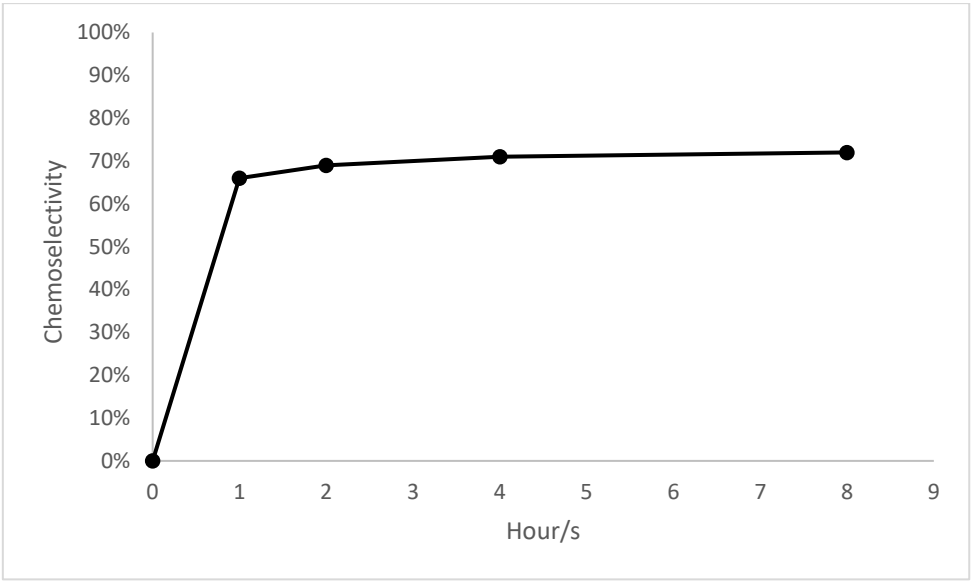


Figure 3.

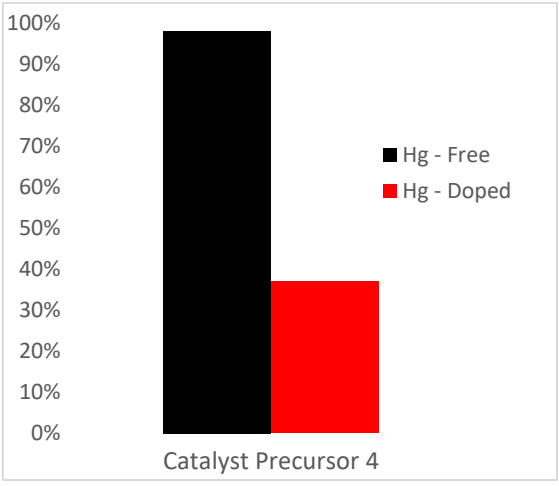


Figure 4